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THE MECHANICAL PRODUCTION OF COLD

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THE MECHANICAL PRODUCTION OF COLD

BY

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PREFACE

THIS book is a reprint of "Howard" Lectures on the Mechanical Production of Cold, delivered before the Society of Arts in 1897, with additions and corrections which show the advances of the past eleven years and bring the accounts of machines and processes into accord with the practice of the present day. In its main features the art of refrigeration has undergone little change in that time. But notable progress has been made in some directions, and this has required the introduction of a good deal of supplementary matter.

In the new portions the separation of oxygen from nitrogen in air, by condensation under extreme cold, is dealt with in some detail. This process, which is due for the most part to the genius of Linde, has become important in the commercial supply of oxygen and also as a step in the manufacture of nitrogenous manure. In the theoretical treatment of refrigerating machines the investigations of Dr Mollier have been specially fruitful. The Appendix will be found to contain an account of useful graphic processes with which he has enriched this branch of technical thermodynamics.

In expanding the book the original form of lectures has been retained, as being appropriate to the intended method of treatment. A general account of refrigeration is given, but it is chiefly on the thermodynamic aspect of the subject that stress is laid.

From this point of view a refrigerating machine is essentially a contrivance for pumping up heat from a place that is comparatively cold to a place that is comparatively warm, and the question of primary interest is how to do this pumping with the least expenditure of power. We are concerned with the theoretical limits to the economy of power that hold in ideal refrigerating processes, and with considerations as to how nearly the actual conditions under which refrigeration is carried out will allow these limits to be approached when one or another type of real machine is employed. The lectures are in great part an attempt to make this side of the subject intelligible without unnecessary mathematics.

In preparing them I obtained much information from Dr Linde, Professor Schröter, Mr Windhausen, Mr Osenbrück, Mr Lightfoot, Mr Hesketh, Mr Sterne, Sir Alfred Haslam, Professor Sir James Dewar, and the late Sir Frederick Bramwell. To many of these gentlemen I am additionally indebted now, especially Dr Linde, Mr Lightfoot, Mr Hesketh and Sir James Dewar. Dr Mollier, Mr Murray of the British Oxygen Company, Sir William Ramsay, and Sir Philip Watts have also most kindly helped in various ways to make the work more complete.

I have also to thank the authorities of the Society of Arts for permission to use material which appeared in the *Journal* of the Society.

J. A. EWING.

August, 1908.

The changes in the Second Edition are mainly the correction of certain *errata* and the clearing up of points in which the original text was somewhat obscure.

J. A. E.

March, 1919.

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LECTURE I.

Preliminary.

FROM the terms of the Howard Bequest, it appears that these lectures are primarily intended for the discussion of some application of thermodynamics. Previous holders of the Howard Lectureship have dealt with the generation and transmission of power. I have been led to select the subject of mechanical refrigeration on the double ground that it is one of the most interesting and comparatively novel applications of power, and that it is further intimately connected with the conversion of heat into work, inasmuch as it is a reversal of the operation by which heat is converted into work—it is a conversion of work into heat, effected in such a way as to produce cold.

Its industrial importance is a matter on which I need not take up your time by dilating. One of its earliest and largest applications is to brewing. It is only by means of mechanical refrigeration that the great modern breweries have become possible. Moreover, it has revolutionised the industry which relates to the distribution and sale of ice. It has given us a product which is not only better than that which nature herself has provided, but can be sold at a price with which natural ice cannot in general compete. It has further created an enormous new industry in the transport and storage of the perishable necessaries of life in a cold state. Perhaps some of us are scarcely aware how much we are indebted to it in this respect. It is open to conjecture that we sometimes owe something to mechanical refrigeration for the supply of that "prime old English beef and mutton" for which we, in any case, pay home prices. It has given us many luxuries, such as paraffin wax, photographic films, and ice rinks. It has given us other things which one would hesitate to describe as luxuries, such as oleo-margarine. The commercial importance of mechanical refrigeration is indicated by the fact that there are two journals exclusively devoted to the subject, the American *Ice and Refrigeration*, the German *Zeitschrift für die gesammte Kälte-Industrie*. The first of these is for the most part severely practical, but is garnished with the shrewd remarks and occasional personalities which are characteristic of the Transatlantic Press. The other is, in its way, just as distinctly national, and fills one with a sense of the lead which Germany has over us in the matter of technical education. A great part of it is occupied by articles of the most substantial kind dealing with points in the thermodynamic theory of refrigeration—articles on which most English engineers would look askance. Not a few of its pages bristle with differential equations.

The subject is pre-eminently scientific as well as practical. In its whole development it has been guided to a remarkable degree by theory, and this has weighed with me in choosing it for treatment in these lectures. We may contrast it in this respect with the development of the steam-engine. That development, in its early stages, owed little or nothing to theory; it took place mainly by an empirical process. Heat-engines were brought to a considerable degree of perfection before even the doctrine was accepted of the mechanical equivalence of heat and work. The case is different with mechanical refrigeration. At every step of the process we find the influence of scientific ideas. No part of it has taken place except under the direct guidance of physical science. If we turn to the writings of inventors on the subject—to the papers of Kirk, Coleman, Lightfoot, Linde, and Windhausen—we find the constant influence of scientific modes of thought affecting and directing their inventions. I may quote in this connection language which was used by Sir Frederick Bramwell in the discussion of a paper by Mr Coleman, read before the Institution of Civil Engineers in 1884. Sir Frederick Bramwell then said: "There probably never had been a paper submitted which made more perfectly clear the necessity that the successful engineer of the present day, and still more the successful engineer of the future, must be a man competent to apply to the pursuit of his profession the highest scientific truths. The subject," he continued, "showed how the very utmost results of thermodynamics were applied in practice for common use."

I propose, first, to go into a few general considerations regarding the thermodynamical basis on which stand all the practical processes of mechanical refrigeration. These considerations may appear rather dry, but they are essential to an understanding of the subject.

Two General Methods.

Broadly speaking, the methods that are employed for the production of cold may be classified under two heads, the second of which is by far the more important in practice. There is, first, the production of cold directly by the agency of heat, or, in other words, the expenditure of heat for the production of cold, and, second, the production of cold by the expenditure of mechanical work. It is by the expenditure of mechanical work that nearly all modern refrigeration is carried out, namely by compressing a gas or a vapour and afterwards allowing it to expand under conditions which allow it to absorb heat from the thing that is to be cooled. In general this mechanical work is, in its turn, obtained by the agency of heat, a steam-engine or other heat-engine being used to drive the refrigerating machine. In such cases we may be said to apply heat indirectly to produce cold, the heat being used first to produce mechanical power, which is then applied for the production of cold. Examples are of course found where some other source of mechanical power, such as water power, is applied, and where, therefore, the agency of heat in the prime mover does not come in at all. But in almost every practical example of refrigeration you find that heat is operative—that at one end of the chain you have the expenditure of heat going on, and at the other end you have the production of cold. Mr Richmond, an American engineer who has written some highly interesting and suggestive papers on the subject, has remarked that if a student beginning to observe the process without any *a priori* ideas were to place himself outside an ice-making factory the first thing he would notice would be that coal goes in at one door and ice comes out at the other.

The Production of Cold: Idea of a Heat-Pump.

Now, what does this phrase, the production of cold, really mean? It implies, in the first place, the reduction of the temperature of a body below the general level of temperature of the surroundings. It further implies the maintenance of the temperature of a body at a lower level of temperature than the surroundings. Consequently, it means the continued extraction of heat from a body whose temperature is already below the temperature of bodies in its neighbourhood. For example, if a cold storage room is being maintained at a temperature of say 18° Fahr., there must be a continual extraction of heat from the atmosphere of the room. We must go on continuously pumping out the heat which comes into the room through leakage from outside, and also whatever heat is brought into the room in articles which are carried into it after the temperature has once been reduced. To maintain the low temperature of a cold storage room you must have a continual extraction of heat going on from a thing which is already colder than its surroundings. Precisely the same remark is applicable in the case of a brine tank for the production of ice. The brine has to be maintained at a temperature somewhat lower than that at which water freezes, considerably lower if the process of freezing is to go on at a reasonably fast rate. The heat which comes into the brine from the water to be frozen, the heat which the water gives out when it freezes, and the heat which leaks in from all sources has to be continuously extracted from the brine at this comparatively low level of temperature. What becomes of the heat so extracted? It is not destroyed; it continues to exist as heat; but it is raised to a higher level of temperature and is discharged there. It is discharged by being given up to some substance which acts as a receiver of heat. In all actual cases of refrigeration the substance which absorbs the rejected heat is circulating water, which becomes more or less warmed by the heat which it takes up. The refrigerating machine accordingly works between two temperatures; the lower temperature is that at which heat is taken in from the body which is to be kept cold; and the higher temperature is that at which heat is rejected to the circulating water or other substance which absorbs it. In order that this process may go on we must have an expenditure of mechanical power. Heat is being virtually pumped up from the low level of temperature to the higher level, and is being rejected at that higher level of temperature. This process will not go on by itself; work has to be done to effect it. The work which is expended is itself converted into heat, and hence the whole quantity of heat which is rejected is made up of two elements. It is the heat which has been extracted at the low level of temperature from the thing that is being cooled or kept cold *plus* the heat which is equivalent to the mechanical work which has been expended in extracting it. The conception of a refrigerating machine as a heat-pump, taking in heat at a low level of temperature, and discharging heat at a higher level of temperature, is of fundamental importance. We may compare it to a pump raising water, but with this difference that in the water-pump the quantity that is discharged at the high level is the same as the quantity that is taken in at the low level, whereas in the heat-pump the quantity discharged is augmented by the conversion into heat of the work expended in the process of pumping.

Co-efficient of Performance.

Taking the process as a whole, a quantity of work, which we may call W, is employed to extract at the low level of temperature a quantity of heat, which we will call Q_2. If Q_1 stands for the heat which is given out at the higher level, then these quantities are connected by the equation

$$Q_1 = Q_2 + W,$$

it being understood that the amount of work W is expressed by its equivalent in heat-units. As regards the efficiency of any process of refrigeration, what we are concerned with is the relation between the quantity of heat Q_2 which is taken in at the low level of temperature, and the quantity of work W which is expended in the process. The larger Q_2 is compared with W the more efficiently is the process of refrigeration being carried out. If we take the quantity Q_2, and divide by W, we get a certain figure of merit which is called the co-efficient of performance. In other words, the co-efficient of performance of a refrigerating machine is defined to be the ratio of the quantity of heat which is extracted at the low level of temperature to the quantity of work which is employed in extracting it.

Ideally Perfect Refrigerating Machine.

A fundamental question in the theory of refrigeration is this: What is the highest possible co-efficient of performance that any refrigerating machine can conceivably have? We shall afterwards have to consider to what extent various practical refrigerating machines succeed in approaching this ideal of perfection. But our attention must first be given to the ideally perfect refrigerating machine, that is to say, the machine whose co-efficient of performance is the highest that is compatible with thermodynamic principles. The co-efficient which is calculated for it is one which may be approached, but cannot possibly be exceeded by any real machine. It forms a standard of comparison by which the performance of real machines may be judged, so far as thermodynamic efficiency is concerned. The ideal performance of a refrigerating machine depends simply upon the particular temperatures between which it works. We shall see that under the ideally perfect conditions a simple relationship exists between the heat that is extracted from the cold body and the work that is done, a relationship which can be expressed as a function of the two temperatures between which the machine works, and that the greater the range of temperature is through which the heat has to be pumped up, the smaller does the ideal co-efficient of performance become. This, then, is a point of much practical consequence. We cannot expect, even in the most perfect refrigerating machine, to find so large a co-efficient of performance in a case where the range of temperature through which the heat is to be raised is great, as we may find when the range is small; and practically it becomes of the utmost importance to keep the range of temperature as small as possible, if we wish to effect refrigeration with the least admissible expenditure of power. In other words, we must aim at keeping the thing from which heat is to be taken at a temperature that is no colder than it is necessary for it to be, and we must aim at discharging at as low a level of temperature as may be the heat which is to be rejected, in other words, we must aim at discharging it into something which is as cold as we can permit it to be. We must pump the heat up through no bigger an interval of temperature than is really necessary in order to get the highest co-efficient of performance, so that we may obtain the largest amount of cooling effect from a given quantity of work.

Co-efficient of Performance of an ideally perfect Refrigerating Machine.

The co-efficient of performance of an ideally perfect refrigerating machine is readily found when we recognise that the operation of such a machine is precisely the reverse of the operation of a perfect heat-engine. In a heat-engine (E, Fig. 1) you have the heat coming in from some source of heat at a high temperature T_1, and going out to some cold body at a lower temperature T_2, and in its fall from the high temperature to the low it does a certain amount of mechanical work W. The heat Q_2, which goes out, is less than the heat Q_1, which comes in, by the amount W which the engine converts into work. In the refrigerating machine (R, Fig. 2), the heat comes in at a low temperature, and goes out at a higher temperature, and in order to make it rise from the lower to the higher level of temperature it needs to have work spent upon it. In the case of the heat-engine, it is a familiar principle of thermodynamics that when the greatest possible amount of heat is being converted into work the ratio of Q_1, the heat which goes in, to Q_2, the heat which goes out, will be the same as the ratio of the absolute temperature T_1, at which the heat comes in, to the

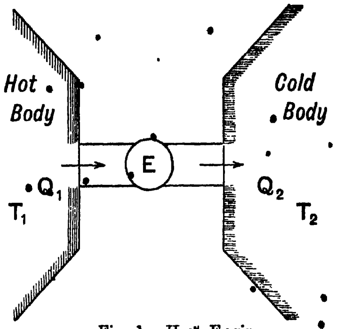

Fig. 1. Heat Engine.

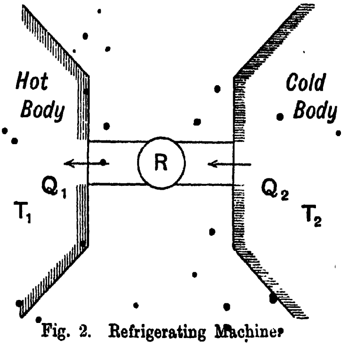

Fig. 2. Refrigerating Machine.

absolute temperature T_2, at which the heat goes out. For brevity you will understand the word temperature in this connection to mean the absolute temperature, that is to say, the temperature expressed on the Fahrenheit scale plus the number 460, or, if you prefer to use the Centigrade scale, the temperature on that scale plus 273. In a perfect heat-engine, which means an engine with the most ideally efficient means of converting heat into work, we have

$$\frac{Q_1}{T_1}=\frac{Q_2}{T_2},$$

and hence W, the work done, which is equal to $Q_1 - Q_2$ is such that

$$\frac{W}{Q_1}=\frac{T_1-T_2}{T_1} \text{ or } \frac{W}{Q_2}=\frac{T_1-T_2}{T_2}.$$

This is the largest amount of work that can possibly be got by allowing heat to pass through a heat-engine from temperature T_1 to temperature T_2. Now turn to the refrigerating machine. The same quantity of work, which was the largest quantity that could be got out of the heat while the heat was flowing down, is the smallest quantity which will suffice to pump it up. The ideally perfect heat-engine is (in the thermodynamic sense) a strictly *reversible* machine, and the work W, which was the work the heat produced when it was used as a heat-engine, is the amount of work which will just suffice to bring the heat through it backwards when we turn it into a refrigerating machine. This may be made plain by the use of a simple argument. Suppose we have (as in Fig. 3) a heat-engine E, and also a heat-pump or refrigerating machine R, both working between a cold body and a hot body. Assume that the heat-engine E is as efficient as is ideally possible. It takes in a quantity of heat Q_1, converts a portion of it into work W, and rejects the remainder Q_2, as heat. Now imagine that that work W is applied to drive the refrigerating machine without any loss of power in the connection between the two. If it were conceivable that the refrigerating machine R were more efficient than a reversed heat-engine, the work spent upon it, W, would extract from the cold body a larger quantity of heat than Q_2, and would reject to the hot body a larger quantity than Q_1. Hence, on the whole, the cold body would lose heat, and the hot body would gain heat without expenditure of work from outside. The two machines, taken together, would form an entirely self-acting agency, for the one produces just enough power to drive the other: and yet the result would be a continuous pumping up of heat from the place where the temperature is T_2 to the place where the temperature has the higher value T_1. That result is contrary to all experience, and would be a violation of the second law of thermodynamics. We cannot have heat flow automatically up hill, that is to say from a colder to a hotter body. It can only be forced to flow up hill by the expenditure of energy. Here, then, we have a *reductio ad absurdum* which comes from imagining it to be possible that the refrigerating machine could be more efficient than a reversed heat-engine of the "perfect" or ideally efficient class, and hence that idea must be abandoned.

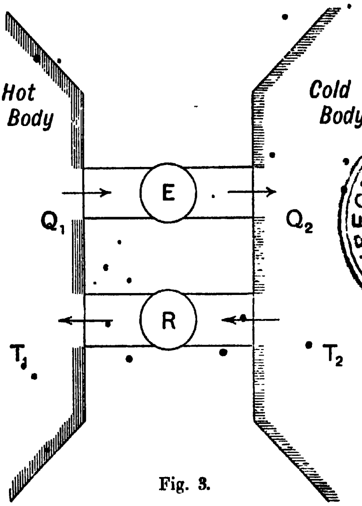

Fig. 3.

DIRECTOR OF INDUSTRIES

The conclusion is that a reversible heat-engine when reversed is the most efficient possible form of heat-pump. In other words, that the largest quantity of work which can be got out of a perfect heat-engine is the smallest quantity of work which will suffice to force heat through the engine in the opposite direction from the cold body up to the hot body, the amount of heat that is transferred being in both cases the same.

Reversibility essential to Perfection.

Reversibility, in the thermodynamic sense, is essential to perfection in the refrigerating machine, just as it is in the heat-engine. The full amount of refrigerating effect, for a given expenditure of work, is obtained only when this criterion is satisfied. Further, to obtain the fullest effect the substance which serves as medium by which the heat is conveyed through the system should take in no heat except when it is already at the lowest level of temperature, and give out none except when it is already at the highest level of temperature. The actions which go on within the machine will be reversible only when there is no unresisted expansion on the part of gas or vapour or any other working substance. Any passage of gas or of liquid through a throttle valve is an essentially irreversible action, and is, therefore, inconsistent with the highest efficiency. Any flow of heat by conduction or radiation between bodies at different temperatures is also an irreversible action. In the ideal reversible cooling machine, just as in the ideal reversible heat-engine, we should have neither unresisted expansion nor flow of heat by contact at any point between a warm and a colder body. In practice we cannot hope to do more than approximate to the ideal of reversibility, but it is easy to imagine a series of operations in which everything is strictly reversible, and in which also the condition is satisfied that all the heat which is taken in shall be taken in at the lowest level of temperature, and that all the heat which is given out shall be given out at the highest level of temperature. Students of thermodynamics are familiar with the cycle of operations which was first described by the French philosopher, Sadi Carnot. This is a strictly reversible cycle for the conversion of heat into work, and we have only to imagine it reversed in order to have, in imagination, an ideally perfect refrigerating machine. You will of course understand that the words "perfection" and "perfect" are used here merely with reference to thermodynamic efficiency, and it is scarcely necessary to point out that there are many other things besides thermodynamic efficiency to be taken into account when we come to estimate the merit of an actual refrigerating machine from the practical point of view. It is not too much to say that a theoretically "perfect" machine would have practical disabilities that would in effect make it useless. In the successful real machine some part of the possible thermodynamic efficiency is sacrificed to secure other valuable qualities, such as speed of working and compactness. But though a better all-round machine is obtained in this way, it is nevertheless useful to bear in mind the ideal limit which the efficiency might attain if the machine were thermodynamically perfect, and to recognise in what respects the real machine's operation departs from this ideal. A comparison of the two may be suggestive of improvement, for it may be possible to approach in some respects nearer the ideal condition without giving up points of practical convenience.

Carnot's Cycle Reversed.

Consider then the ideal engine of Carnot, reversed to form an ideal cooling machine.

Imagine a cylinder and piston (Fig. 4), made of non-conducting material, except that the bottom of the cylinder is a conductor. Suppose further that we may fit to the bottom of the cylinder either the cold body C, from which heat is to be extracted, or a warmer body, A, to which heat may be rejected, or a non-conducting cover, B. At the beginning of the process we have in the bottom of the cylinder a quantity of a substance which we will for simplicity assume to be a liquid, and this liquid is at the same temperature T_1 as the warm body A. The first operation is to apply the non-conducting cover B, and allow the piston to rise. As it rises the liquid begins to evaporate, and its pressure and temperature both fall. Let this go on until the temperature of the substance, which is now a mixture of liquid and vapour, has

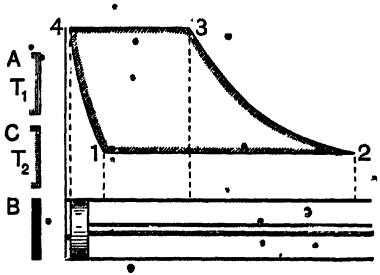

Fig. 4.

fallen to the lower level of temperature, T_2. On the indicator diagram which is sketched above the cylinder in Fig. 4 this part of the process corresponds to the line 4 1. This action has gone on without any introduction of heat from outside—in other words, it is what is called in thermodynamics an adiabatic action. Next, let the non-conducting cover be removed and the cold body be put in contact with the bottom of the cylinder, the contents of which are already at the temperature T_2 of the cold body, and let the piston continue to rise. The substance goes on evaporating under the constant pressure corresponding to the temperature T_2, taking in heat from C. This part of the process goes on at constant temperature and for that reason is called isothermal. It is shown by the line 1 2, which indicates the change from a state in which there is very little vapour and much liquid to a state where much of the substance has been vaporised. We might continue this process until all the liquid has turned into vapour, but it is more convenient to suppose it stopped while there is still some liquid present in the mixture. When the stage 2 has been reached let us replace the non-conducting cover after removing the cold body and begin to force the piston down. This compresses the substance adiabatically, and consequently causes its temperature to rise. Through this process certain changes take place in the proportion of liquid and vapour. If we have a perfectly dry vapour at point 2, then it will be superheated by the compression, but if we have left a sufficient mixture of liquid with the vapour it will remain saturated during compression. In that case the mixture becomes drier as we compress it—that is to say, the proportion of liquid to vapour becomes reduced. This process is continued until, at the point 3, the temperature has risen to T_1. The simplest supposition to make is that we have stopped the process 1 2 at such a point that when we compress the mixture it takes the condition of dry saturated vapour when this process is completed at the point 3. Then apply the warm body A in place of the non-conducting cover and continue the compression. During this final process the vapour is further condensed, giving out heat to A, and remaining at the temperature T_1. The whole cycle of operations is completed at point 4, when the working substance has been brought back to the condition in which we supposed it to be at the first. Observe that in all this process there is only one time when heat is taken in, viz., the stage 1 2, and only one time when heat is being given out, viz., the stage 3 4. While the heat is being taken in the working substance has already been brought to, and is continuously kept at, the temperature of the cold body T_2, similarly, all the while that heat is being given out the working substance is continuously at the temperature of the warm body, T_1. The conditions of reversibility are satisfied. There is no contact between things at different temperatures. In the whole of the action there is nothing of the nature of unresisted expansion. There is no passing through a throttle valve, nothing to interfere with reversibility either as regards the mechanics of the process, or as regards the transfer of heat. If we could make a refrigerating machine act in this way it would be an ideally perfect machine, from the thermodynamic point of view, and its co-efficient of performance would have the ideally highest value.

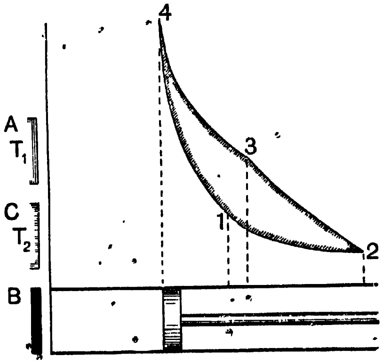

Fig. 5.

In Fig. 5 we have an example of this same Carnot cycle, but with air as the working substance instead of liquid and vapour. The form of the indicator diagram is very different, but the four processes which make up the cycle are the same as before, namely two isothermal and two adiabatic, and the co-efficient of performance, depending, as it does, only on the temperatures, has the same value.

Value of the Ideal Co-efficient of Performance.

We have seen by comparison with the performance of a perfect heat-engine, that in this ideal limiting case $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$, where Q_1 is the heat rejected into the warm body A, at the absolute temperature

T_1, and Q_2 is the heat taken from the cold body C at the absolute temperature T_2. Hence $\frac{Q_1 - Q_2}{T_1 - T_2} = \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$. But $Q_1 - Q_2$ is W, the amount of work spent on driving the machine. Consequently the co-efficient of performance, which is the ratio of the heat taken in to the work done, or $\frac{Q_2}{W}$, is in this ideal case equal to $\frac{T_2}{T_1 - T_2}$. It follows that in a perfect refrigerating machine the performance would be entirely dependent on the two temperatures, and would be the same whatever working substance was used in the cylinder. This ideal co-efficient, $\frac{T_2}{T_1 - T_2}$, is a number much greater than unity in most cases. So long as the range of temperature, $T_1 - T_2$, is not very great, the number which we get by dividing T_2 by $T_1 - T_2$ will be large. In the table a series of numbers are given which show the values of this expression $\frac{T_2}{T_1 - T_2}$ for various assumed temperatures, which are stated however not as absolute temperatures but on the usual Fahrenheit scale. These are the ideally highest co-efficients of performance which can be reached in any process of refrigeration, T_2 being the temperature of the place from which heat is being taken, and T_1 the temperature at which heat is being rejected.

Co-efficients of Performance of a Perfect Refrigerating Machine.

Lower Limit of Temperature in Deg. Fah.	Upper Limit of Temperature in Deg. Fah.					
	50°	60°	70°	80°	90°	100°
—10°	7·5	6·4	5·6	5·0	4·5	4·1
0°	9·2	7·7	6·6	5·8	5·1	4·6
10°	11·7	9·4	7·8	6·7	5·9	5·2
20°	16·0	12·0	9·6	8·0	6·8	6·0
30°	24·5	16·3	12·2	9·8	8·2	7·0
40°	50·0	25·0	16·7	12·5	10·0	8·3

For example, suppose you were refrigerating from a temperature of 20° Fahr., and rejecting heat at 60° Fahr., the ideal refrigerating machine would have a co-efficient of performance of 12, that is to say, you could get 12 times as much heat extracted from the cold body as you applied to the machine in the form of work, whereas, if you were pumping up the heat to the higher level of 100° Fahr., and extracting it from the lower level of $-10°$ Fahr., then the amount of heat extracted could not exceed 4·1 times the amount of work done. Taking the perpendicular columns, it is seen how the best refrigerating effect obtainable from a given amount of work depends on the temperature of the thing from which the heat is being absorbed. Taking the numbers horizontally, it is seen how the same quantity depends on the temperature of the condensing water, that is to say, on the temperature to which you are obliged to raise the heat in order to get rid of it.

These numbers will serve not only to show the limiting efficiency, which any real refrigerating machine necessarily falls much short of, but also to illustrate the great advantage that accrues in the process of refrigeration from keeping the range of temperature as narrow as possible, by taking in the heat at as high a level of temperature as is permissible and not raising it to any higher level than is really necessary before it is rejected.

Another way of stating the ideal limit of best performance in the process of refrigeration is to give the number of thermal units capable of being extracted for each horse-power-hour of work spent. To find this we have only to multiply the co-efficient of performance by 2545. For one horse-power hour represents 33000×60 foot-lbs. of work, and taking Joule's equivalent to be 778, the corresponding quantity of heat is $\frac{33000 \times 60}{778}$ or 2545 British thermal units.

Entropy Diagram.

Instead of using the indicator diagram to exhibit any such cycle we shall sometimes find it of very great service to use what is called the entropy diagram. In the entropy diagram, as in the indicator diagram, quantities of heat and work are represented by areas, but one of the co-ordinates of the entropy diagram is the absolute temperature, and consequently the other co-ordinate, the entropy, is a quantity of the dimensions of heat divided by temperature. We may define sufficiently for our present purposes this word "entropy" in the following way. If a substance takes in or gives out heat at any temperature, while changing its state in a reversible manner, the quantity of heat taken in or given out, divided by the absolute temperature at which it is taken in or given out, measures the amount by which the substance changes its entropy. It may be added that we are only concerned with changes of entropy, reckoned from some convenient state of the substance under consideration and that we have no need to attempt any reckoning of the absolute entropy of the substance. It is a convenient practice to reckon the entropy as zero when the substance is in the state of a liquid, and at the temperature 32° Fahr. or 0° Cent. The reckoning is also made per unit of mass of the substance.

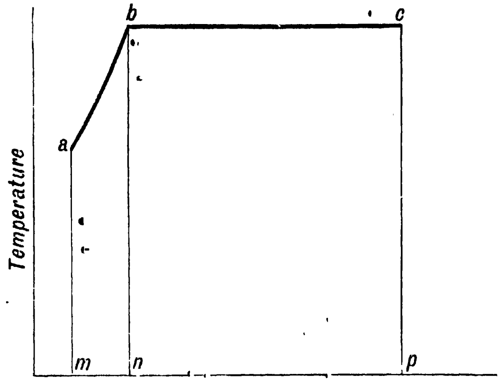

Fig. 6.

Let us consider the changes of entropy that occur when a liquid is first heated from some lower temperature up to the boiling point and then passes from the liquid into the gaseous state. In that case the substance gains entropy in two stages. In the first stage the temperature is rising while heat is being taken in; consequently the process is represented on the entropy-temperature diagram by a line that slopes upwards, such as *ab* in the figure. In the second stage the temperature is constant, and accordingly the line is a horizontal one (*bc*), drawn at a level corresponding to the absolute temperature T at which the change of state occurs, and its length, which measures the gain in entropy, is $\frac{L}{T}$, where L is the "latent heat." For L is the heat taken in during this stage, and T is the absolute temperature at which it is taken in, and consequently by our definition the entropy has changed by the amount $\frac{L}{T}$. Notice further that the area under the line bc, namely the rectangle $nbcp$, measures the heat taken in, for that area is the length bc into the height or $\frac{L}{T} \times T$, which is L. Similarly it may easily be shown that the area under the sloping line ab measures the heat taken in during the earlier stage, when the liquid was getting warmed up to the boiling point. (See Appendix A.)

Again, if a substance expands adiabatically, so that no heat is taken in or given out, there will by the definition be no change of entropy, though the temperature falls. Consequently this process would be represented in the diagram by a vertical straight line, coming downwards. Similarly a vertical straight line going upwards represents a process of adiabatic compression.

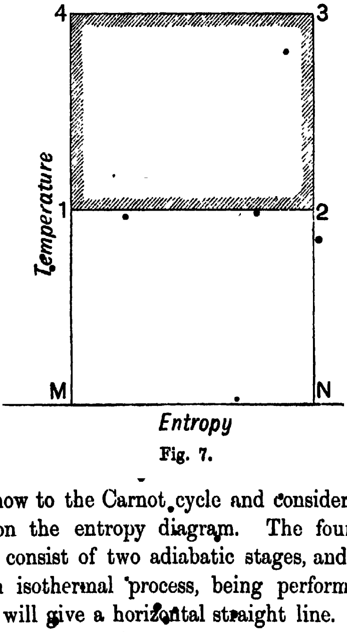

Fig. 7.

Go back now to the Carnot cycle and consider how it will be represented on the entropy diagram. The four stages of the Carnot cycle consist of two adiabatic stages, and two isothermal stages. Each isothermal process, being performed at constant temperature, will give a horizontal straight line. Each adiabatic process will, as we have just seen, give a vertical straight line. The diagram for the Carnot cycle will therefore consist of two vertical lines and two horizontal lines (Fig. 7), and this will be the form of diagram whatever be the substance that is taken through the Carnot cycle. The lettering in this diagram corresponds, for the various stages, to that used in the indicator diagram given before. The indicator diagrams are very different in Figs. 4 and 5, but the entropy diagram of Fig. 7 applies equally to both. We shall have occasion to make considerable use of entropy temperature diagrams later when we discuss the action of various substances in refrigerating machines.

Refrigerating Machines with Separated Organs.

In this imaginary cycle we have supposed the whole of the action to be going on within a single vessel. The cylinder serves not only for the expansion and compression of the substance, but also as condenser and evaporator. In actual refrigeration it would be impracticable to have all the different parts of the process performed in a single vessel. The imaginary engine of Fig. 3 resembles those primitively simple living things in which a single organ serves all the purposes of stomach, heart and brain. As you ascend in the scale of life you find more and more complexity, separate organs being evolved to discharge separate functions. From the primitive Carnot engine with its single organ we may proceed to imagine a more practicable refrigerating machine in which each of the four stages of the process has an organ to itself. Suppose there is, as in Fig. 8, a separate cylinder for compression, and another for expansion, a separate vessel C in which the substance is taking up heat, and another A, in which it is giving out heat. You may conceive of C as a tank containing brine which is to be kept cold, and A as a condenser in which the heat given out by the working vapour as it condenses is absorbed by circulating water. The condensed vapour passes from A into the expansion cylinder, and is adiabatically expanded there until the temperature falls to that of C. It is then discharged into C, and is further vaporised, thus taking up heat from the brine; it then passes on to the compression cylinder, is adiabatically compressed until its temperature rises to that of A, and is then delivered to A, being isothermally compressed while it condenses there. Thus a cycle identical with that of Fig. 3 might be gone through with the engine of Fig. 8, in other words we might have a theoretically perfect refrigerating process with separate cylinders for compression and for expansion, and separate vessels for evaporation and for condensation.

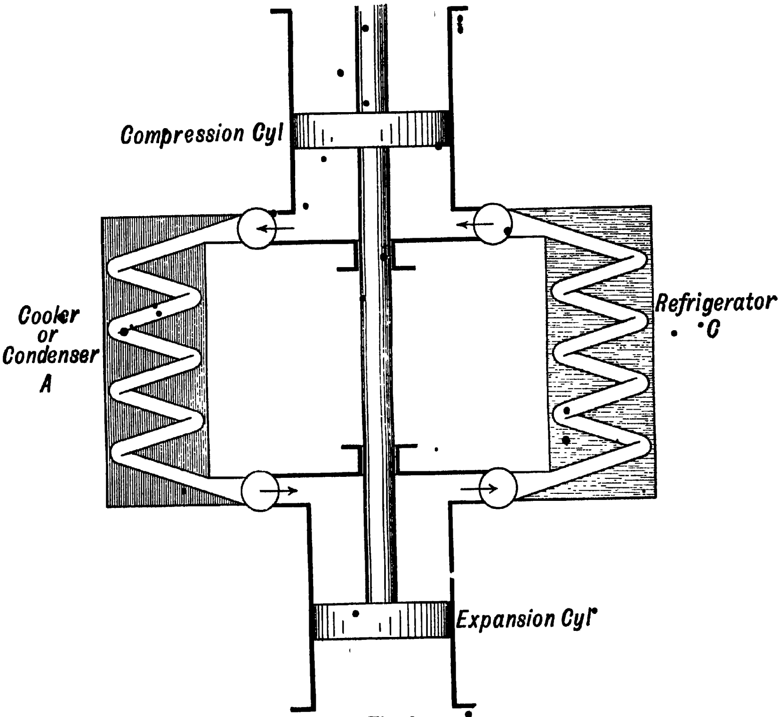

Fig. 8.

In practice, however, the refrigerating machine as it exists does not have all these organs. When we are dealing with liquid and vapour, the universal practice at the present time is to omit one of the organs, namely, the expansion cylinder, and in consequence of that we have an action which is not identical with the Carnot action, but is thermodynamically a less perfect action. The condensed vapour is allowed simply to stream through a throttle valve from the condenser to the refrigerator, without doing work on the way in an expansion cylinder. The reason for this is that we get a simpler machine without very much loss of thermodynamic efficiency, by omitting to save the work done in expansion. We shall discuss this point more fully in a later lecture, but I may say now that two things follow from this modification of the cycle. In the first place, the amount of work which has to be expended on the material in carrying it through the whole cycle becomes slightly greater because the work which would be recovered in the expansion cylinder is not recovered, and, in the second place, the amount of heat which is extracted from the cold body C becomes somewhat less, because the liquid is not made cold by expansion before it enters C, and consequently it carries with it a quantity of heat into the refrigerating chamber or tank, and so diminishes the amount of net or effective refrigeration.

Use of Regenerator.

The Carnot cycle, carried out in its entirety, which it never is in practice, is one means by which we might have a perfect refrigerating machine, and get the theoretically greatest amount of refrigeration from a given expenditure of work. But there is one other means by which we might, in theory, have a perfect refrigerating machine. Besides the Carnot cycle there is one, and only one other possibility of getting thermodynamical perfection. It is by taking advantage of an old invention made in 1837 by a Scottish minister, the Rev. Robert Stirling. Students of thermodynamics are familiar with the Stirling hot-air engine, in which the working substance is made to pass alternately forwards and backwards through what is called a regenerator, a body packed with a quantity of wire gauze, or some other material capable of taking up heat from the working substance when it passes through it in one direction, and then giving back that heat to the working substance when it passes through it in the other direction. In the Carnot cycle the characteristic is that the change from high temperature to low temperature, and again from low temperature to high temperature, is performed in each case by adiabatic expansion or adiabatic compression. In the Stirling engine the corresponding changes are performed by passing the working substance through the regenerator, and the characteristic of that action is that the heat which is deposited by the substance in the regenerator is taken up again—in theory entirely, in practice partly—as it comes through it in the other direction.

By an action of this kind it is possible to have thermodynamically the equivalent of the Carnot cycle, although the operation is in this respect different. The indicator diagram given by a gas in passing through a perfect cycle in which a regenerator is used in place of the two adiabatic stages, is given in Fig. 9.

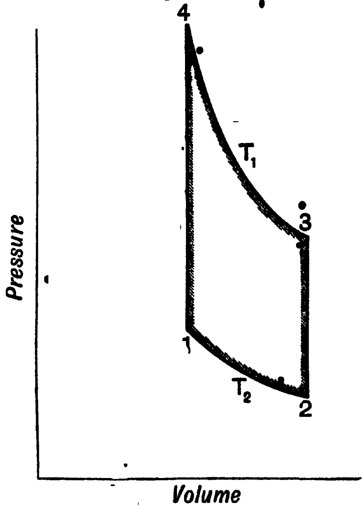

Fig. 9.

Fig. 10 is the corresponding entropy diagram. In both figures

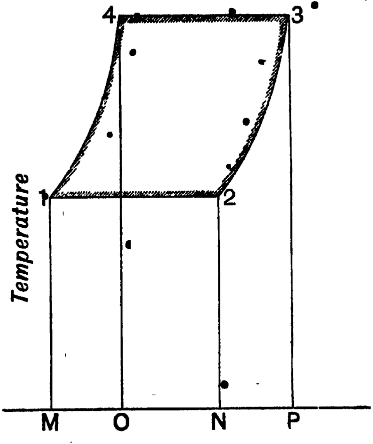

Fig. 10.

the lines 4 1 and 2, 3 show gas passing through the regenerator, giving up heat to it when passing in one direction, and recovering that heat when passing in the other. If all the heat deposited in the regenerator were picked up again, and if the cycle were in other respects reversible, it would be as efficient as the Carnot cycle. In practice, however, a regenerator cannot be made to store and restore heat without loss.

In one of the earliest of practical refrigerating machines a regenerator was actually used. Kirk's air machine, which will be mentioned more particularly in my next lecture, is interesting as embodying an endeavour to approximate to the ideal performance not on the lines of the cycle of Carnot, but on those of Stirling, using a regenerator.

The Areas in the Entropy Diagram.

The entropy diagram has this great merit, that it shows at a glance, not only the work which is being expended on this substance in taking it through the cycle, but also the amount of heat that is taken up at one part, and the amount that is given out at another. In the Carnot cycle (Fig. 7), and again in the Stirling cycle (Fig. 10), we have not only the area of the figure 1, 2, 3, 4 representing the amount of work that is expended on the substance, but the area underneath, namely, the rectangle 1 N represents the amount of heat which is taken out of the cold body, and the area 4 N in Fig. 7 or 4 P in Fig. 10 represents the amount of heat which is rejected to the warmer body. Thus the diagram shows by three different areas the three quantities which we are concerned with, the quantities which I have expressed by the letters Q_1, Q_2, and W, or $Q_1 - Q_2$.

Again, the entropy diagram shows plainly how important it is to make the range of temperature narrow, and especially to keep the cold body no colder than is necessary. In the entropy diagram of Fig. 11, an area representing one definite quantity of work is sketched in three different conditions of temperature, always having the same upper level T_1, but with three different values of the lower temperature T_2. In other words the diagram relates to three ideal cases of refrigeration in all of which the heat rejected by the cooling machine is thrown off at the same level of temperature, namely T_1, but the temperature of the cold body, from which heat is to be abstracted, is comparatively high in case (*a*), lower in case (*b*) and lowest of all in case (*c*). In all three cases the same amount of work is supposed to be spent in driving the machine. The diagram shows well the great differences in refrigerating effect,

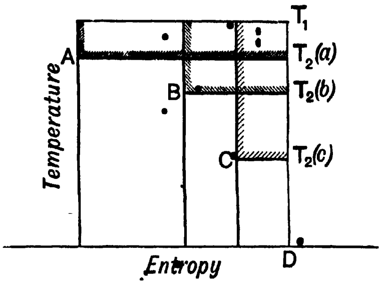

Fig. 11.

due to differences in the cold temperature. The amount of refrigeration which the same amount of work is theoretically capable of performing is shown by the rectangle C D in the third case, by the larger rectangle B D in the second, and by the very much larger rectangle A D in the first. If we allow the level from which we pump up the heat to be low (as at *c*), we get only this very moderate amount of refrigeration C D. If we can allow it to be high, not very far from the temperature at which we have to reject the heat (as at *a*), we get with the same expenditure work the enormously larger quantity of refrigeration represented by the rectangle A D.

Importance of keeping the Range of Temperature as small as possible.

The practical moral of this is plain. Not only should the cooling water be as cool as possible, and not only should the working substance be heated to no higher temperature above the level of the cooling water than is necessary to secure a sufficiently rapid discharge of heat, but, besides that, we should avoid having the lower limit any lower than can be helped. Suppose, for instance, that the problem is one of cold storage, and we are using ammonia as our refrigerating medium ; if we allow the store to be kept cold by the direct evaporation of ammonia in pipes which are placed in the store, we shall in general be absorbing heat at a higher temperature than if we were first of all to apply the evaporation of ammonia to cool a tank of brine, and then make the cold brine circulate through the store. In the second case, the communication of heat to the working substance is less direct, for there are two steps to be passed. The heat has to go from the air of the store into the brine, and then from the brine into the ammonia, and in each of these steps there must be some difference of temperature in order that the heat may flow across the conducting surface which separates the one substance from the other. In the other case there is only one step, the air giving up its heat directly through the pipes to the ammonia, and, consequently, the extent by which the ammonia needs to be lower in temperature than the air of the cold chamber may be expected to be less[1]. Anything that lessens this interval of temperature lessens the amount of work that must be spent in maintaining the refrigeration. I do not, of course, mean to suggest that there are not circumstances in which brine circulation is advantageous. There are many practical points to be considered besides this question of thermodynamic efficiency.

Direct Application of Heat to Produce Cold.

I have still something to say about the production of cold by the application of heat instead of by the application of mechanical power. There are certain types of refrigerating machines where there is no visible application of mechanical power at all; where you are simply giving heat to the machine from a high temperature source, and the result of this is to pump heat up from a low temperature to another temperature at which it is rejected. The ammonia absorption machine is a familiar practical example of this class. There you have three temperatures to consider; the temperature T, at which the high-temperature heat is supplied, the low temperature T_2 of the cold body from which the heat is being extracted, and the intermediate temperature T_1, at which heat is being rejected. Diagrammatically we may represent the matter in this way (Fig. 12). Any machine which directly applies heat to produce cold, may be regarded as equivalent to a combination of motor, or heat-engine, and refrigerator, or heat-pump.

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[1] It is, however, possible to arrange matters so that the use of brine may actually reduce instead of increasing the interval of temperature. If brine is made to drip over the ammonia pipes, and air is blown past the dripping brine, the air may be brought nearer in temperature to the ammonia than it usually is in direct ammonia circulation.

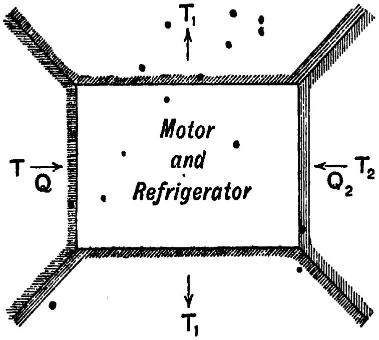

Fig. 12.

A quantity Q of high-temperature heat goes in at one place, a quantity Q_2 of low-temperature heat is thereby caused to go in at another place, and there is an intermediate temperature T_1 at which heat is rejected. The heat Q_1 which is rejected at this intermediate temperature is equal to the sum of Q and Q_2, for there is no work done by the machine or spent upon it, as a whole. An important practical question with regard to such a machine, is what is its ideally best performance. What is the ratio which exists in the most favourable possible circumstances between the high-temperature heat Q that goes in at one end, and the low-temperature heat Q_2 which is thereby extracted from the cold body at the other end? If we imagine the machine to consist of a perfect heat-engine driving a perfect refrigerating machine, it is easy to calculate this ratio when the three temperatures are assigned. The quantity of heat Q supplied at temperature T and working between that temperature and T_1, is capable of doing an amount of work W such that

$$W = \frac{Q(T - T_1)}{T}.$$

Then this work W, applied to drive a perfect refrigerating machine which works between the temperatures T_2 and T_1, is capable of absorbing from the cold body an amount of heat Q_2 such that

$$W = \frac{Q_2(T_1 - T_2)}{T_2}$$

since $\frac{T_2}{T_1 - T_2}$ is the coefficient of performance. Hence the greatest refrigerating effect which such a combination of perfect heat-engine and perfect refrigerating machine could produce is given by the equation

$$Q_2 = \frac{Q\,T_2(T - T_1)}{T(T_1 - T_2)}.$$

But the question arises, is there any imaginable way of applying the heat Q so as to produce a greater refrigerating effect than this, the temperatures remaining as before? The answer is no. The combination of a reversible heat-engine with a reversible heat-pump affords a means of utilising heat for the production of cold, which cannot be surpassed in efficiency by any other imaginable contrivance. To prove this it is only necessary to apply the method of argument already used, and to think of the combination as reversed, delivering heat Q to the body at T, and also delivering heat Q_2 to the body at T_2. Then, if any other contrivance could be more efficient, it would, using the same high-temperature heat Q, remove more heat than Q_2 from the cold body. Hence, if both machines were working together, on the whole the cold body would lose heat, while, on the whole, the hot body would lose none. In other words, we should then have the impossible result that heat would, without expenditure of work from outside and by an agency that is purely self-acting, pass from the cold body at T_2 to the warmer body at T_1, the intermediate temperature. The conclusion is that no type of refrigerator using heat directly as the agent, such, for instance, as an absorption machine, can give a higher ratio of Q_2 to Q than is expressed by the above equation. In point of fact, no absorption machine gives nearly so good a return for its heat as this, for the absorption machine has an action that is not by any means reversible, and, moreover, it rejects heat at temperatures higher than the temperature of the circulating water. Any heat rejected at a temperature higher than T_1 implies a sacrifice of efficiency.

The entropy diagram may be used to illustrate the most effective means of applying heat to produce refrigeration. In

Fig. 13 the rectangle *RO* is drawn to represent the high-temperature heat which is supplied, and the rectangle RT_1 shows the work

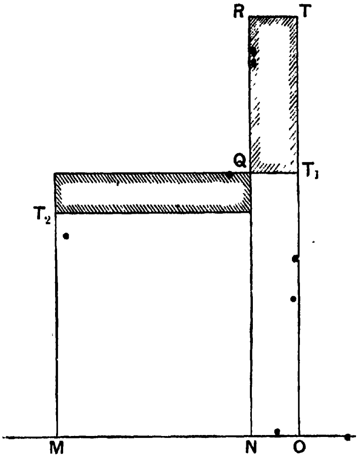

Fig. 13.

which would be done by a perfect heat-engine receiving heat at *T* and rejecting heat at T_1. Let T_2 be the temperature of the cold body from which heat is to be extracted. Draw a rectangle QT_2, equal in area to RT_1. Then the rectangle T_2N measures the amount of refrigeration which can, under ideally favourable conditions, be effected by the heat *RO*. When *T* is high, and T_2 not much lower than T_1, it is clear that the supply of heat *RO* may be much less than the refrigerating effect T_2N. Ideally, therefore, a given quantity of heat in coming down to the intermediate temperature from the high temperature may cause much more than an equal quantity of heat to be pumped up to the intermediate temperature from the low temperature. In practice, however, absorption machines pump up less heat than they take in, because they fall much short of the ideal in efficiency.

A mechanical analogy, which is indicated in Fig. 14, may help to make the ideal process plain. Here a quantity of water, *M*, is supplied at a high level, *H*, and does work in coming down to a lower level, H_1. This work is applied to raise another quantity of water, M_2, from a still lower level, H_2, up to H_1. The water that has come down from the higher level, doing work, as well as the water that has been raised from the low level, is allowed

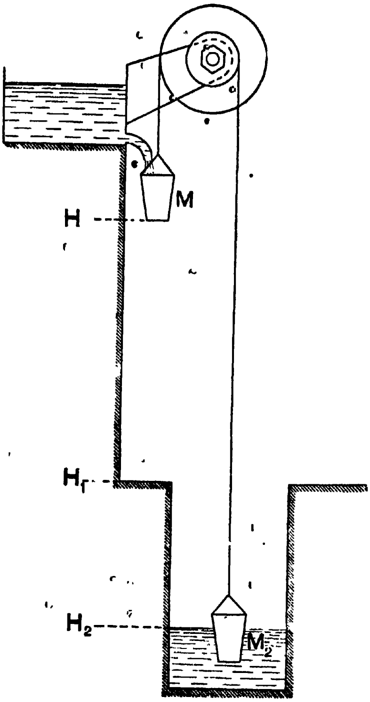

Fig. 14.

to flow away at the level, H_1. The quantities are connected by the equation

$$M(H-H_1)=M_2(H_1-H_2).$$

Comparing this with the equation given above, which may be written

$$\frac{Q}{T}(T-T_1)=\frac{Q_2}{T_2}(T_1-T_2),$$

we see that if temperature be taken as the analogue of level, the thing which is the analogue of quantity of water is not simply heat, but heat divided by the temperature at which it is supplied: in other words, entropy.

The Refrigerating Machine as a Means of Warming.

An interesting fact is to be noted before we leave the consideration of Fig. 12. The combination of heat-engine and heat-pump imagined there has the effect of delivering to the middle region at T_1 a quantity of heat Q_1 equal to $Q + Q_2$. It is clear that Q_1 is necessarily greater than Q and may be very much greater. Now, suppose the space at T_1 is a room which is to be kept somewhat warmer than the outer atmosphere, and that the temperature outside is T_2. A comparatively small quantity of high-temperature heat, Q, applied in this way, will serve to deliver to the room a very much greater quantity of low-temperature heat. This was pointed out as early as 1852 by Lord Kelvin[1], who showed that in the warming of rooms it would be in theory much more economical to apply the heat got from burning coal in this way, than by directly discharging it into the room that is to be warmed. The value of high-temperature heat is in great measure wasted if we allow it to enter a comparatively cold substance. The way to utilise it to the best advantage would be to drive a heat-engine, and let that in turn work a heat-pump, which would lift a much larger quantity of heat from the surrounding level of temperature through the small range that is required. To use a coal fire in warming a room is, from the thermodynamic point of view, a piece of prodigality, and it would still be prodigal even if we did not, as we do, allow most of the heat to escape by the chimney. It is at least of some theoretical interest to recognize that even the most economical of the ordinary modes of heating buildings, with all their practical advantages in respect of simplicity and absence of mechanism, are in the thermodynamic sense spendthrift modes of using fuel.

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[1] *Proc. Phil. Soc. of Glasgow*, vol. iii. p. 269, or *Collected Papers*, vol. i. p. 515.

LECTURE II.

Classification of Refrigerating Machines generally.

In the first lecture I dealt with the process of refrigeration from the point of view of abstract thermodynamics. We have now to consider the development of actual refrigerating machines. We may classify such machines by reference to the particular working substance they employ. A broad distinction may be drawn between machines which use air as their working substance, and those which use a liquid, which is alternately vaporised and liquefied during the cycle of operations. Generally speaking, in this second class of machines the liquid which is used is one whose vapour pressure is higher than the pressure of the atmosphere, under the actual conditions of temperature at which the machine works. If we take, for instance, ammonia or carbonic acid as the liquid which is alternately liquefied and vaporised, we find that under the conditions of temperature within which such machines work, the pressure of the vapour is higher than the atmospheric pressure. But it is quite possible to use a liquid which can only be vaporised by submitting it to a lower pressure than that of the atmosphere under the given conditions as to temperature. Water is an instance in point. At the temperatures at which refrigerating machines work water can only be vaporised by subjecting it to a much lower pressure than that of the atmosphere. Consequently, when water is the working substance, as it is in certain machines, the whole action is taking place in what is relatively speaking a vacuum. It has to take place in chambers which are maintained at a pressure much below the pressure of the atmosphere, and consequently machines using water as their working substance are frequently spoken of, for this reason, as "vacuum" machines. This name is applied as a general title to machines in which the vapour pressure is considerably less than the atmospheric pressure throughout the cycle.

Further, when a vaporised liquid is used for working substance we may either adopt simply mechanical compression as the means of restoring the vapour to the liquid state, or we may adopt in place of mechanical compression a chemical action between the vapour and some other substance which has an affinity for it. This alternative gives rise to the grouping of machines under the title of "compression" machines on the one hand or "absorption" machines on the other. We classify as absorption machines those in which a quasi-chemical action or species of solution goes on as a substitute for the mechanical compression used in the other vapour machines. In absorption machines there is usually a direct application of heat instead of mechanical power, and this forms another distinction between such machines and those of the compression type.

Then we may classify machines of the vapour-compression type according to the particular vapour which they employ, as ammonia, carbonic acid, sulphurous acid, or ether machines.

We may also divide air-machines into two groups, in one of which the same volume of air is made to pass again and again through a cycle of operations without leaving the machine. In this group of machines the air is confined in vessels which allow it to be used throughout its working cycle of operations at a pressure higher than that of the atmosphere. Such machines are called closed cycle machines to distinguish them from the ordinary refrigerating machines employing air, in which the air is discharged from the machine at atmospheric pressure, and air is taken back again to the machine at atmospheric pressure.

Development of Air Machines: Historical Sketch.

Vapour compression machines—that is machines which employ compression to liquefy a vapour and make use of its alternate condensation and re-evaporation, under two pressures and therefore at two temperatures—form now-a-days by far the most important class of refrigerating machines. We shall discuss them later; but first I have to speak of machines which employ air as the working substance. Such machines filled an important place in the history of the development of mechanical refrigeration, and they are still doing useful work; though the more efficient and more compact machines of the vapour compression type, using ammonia or carbonic acid, have now to a great extent driven them out of the field.

The first form of air-refrigerating machine of which there is any notice was one invented by Dr Gorrie at New Orleans about 1845. The earliest published account of it which I have been able to find dates from 1849. It was patented about that time in England, and a machine was constructed with the intention of using it to make ice. Sir William Siemens was asked to examine this machine professionally because it had failed to do what was expected of it, and in 1857 he wrote a report in which he criticised the machine point by point, indicating the various reasons why its duty was less than had been anticipated, and showing what were the several respects in which it might be improved. This report was afterwards published in the Proceedings of the Civil Engineers as a contribution to a discussion on refrigerating machinery[1]. Dr Gorrie's machine had a compression cylinder in which the air was compressed, and from which it passed into a chamber which was kept cool by surrounding water. This chamber or receiver was maintained at a pressure of about 15 lbs. per square inch above the pressure of the atmosphere. The air was partly cooled during compression by the injection of water, so that what passed on to the receiver was really air and water together. The air was further cooled in the receiver by the application of cold water outside, and then it passed on to another cylinder, in which it was allowed to expand down to something like atmospheric pressure. While it was expanding it was mixed with a certain quantity of brine which was injected into the expansion cylinder. By being expanded the air became much cooled and its low temperature was communicated by direct contact to the brine which was mixed with it in the expansion cylinder. The air leaving the expansion cylinder was allowed to escape to the atmosphere, while the brine, which had been cooled to about 20° Fahr., was conveyed into a tank, and was usefully applied to ice-making or other refrigerating purposes.

Siemens pointed out that by no means the whole of the cold which was produced in this machine was usefully applied. The air was allowed to escape to the atmosphere at the low temperature which it had reached in expansion, and the only part of the cold which could be said to be usefully applied was that part which was communicated to the brine during the expansion of the air. One of Siemens' suggestions was that the cold air, instead of being simply allowed to escape to the atmosphere, should be made to give up its heat to the atmospheric air which the engine was taking in for its next stroke, and he proposed what became known as an interchanger for this purpose. According to this proposal, the cold air before being liberated should pass through a series of pipes, outside of which should pass the air which was coming to the compression cylinder from the atmosphere; in this way most of the cold would be saved which was being allowed to go to waste through the direct discharge of the chilled air into the atmosphere. This interchanger of Siemens is the earliest example we have of what may be called the regenerative principle as applied to refrigerating machines. If we had time to go into the history of the subject in detail, we should find substantially the same idea cropping up at various dates, and being applied in various ways. We find it in ammonia absorption machines, and we find it also taking a very practical form in some of the latest developments of the art of producing cold, which I shall have to refer to in my last lecture.

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[1] *Min. Proc., Inst. C.E.*, vol. lxviii., 1882, p. 179.

Another point to which Siemens drew attention was this. In Dr Gorrie's machine there was placed between the chamber containing the compressed air and the expansion cylinder a regulating valve, which was only partially open, so that the air lost a good deal of its pressure as it passed from the chamber into the expansion cylinder. Siemens pointed out that the introduction of this throttle valve was entirely wrong from the thermodynamic point of view, and that it resulted in much loss of refrigerating effect. When air passes through a throttle valve it scarcely falls in temperature at all, but the reduction of pressure puts it in a worse condition for being chilled by expansion in the cylinder, since there is now a smaller range of pressure through which it can expand. A third point which the report of Siemens dealt with in detail was the influence of the moisture contained in the air on the efficiency of the apparatus. The whole report is a document of great interest to any student of the subject as being the earliest criticism of a real refrigerating machine from the point of view of the mechanical theory of heat.

There was, however, a paper some years earlier than this by Lord Kelvin, which ought to be referred to in any historical sketch of the subject, however brief[1]. In 1852 the subject was engaging the attention of Kelvin, and also of another great founder of applied thermodynamics, Rankine. Kelvin describes, in language which is almost precise enough for a patent specification, a machine substantially the same as that which afterwards became a practical success in the hands of Coleman and other inventors. Indeed, Mr Coleman, in his description of his well-known machine, admits frankly that he owes the inspiration of it to Lord Kelvin.

Kirk's Regenerative Air Machine.

But, before we pass on to see what fruit came from this important paper, we have to deal with another type of air machine, which was reduced to practical form by Dr Alexander Kirk in the year 1862. Kirk's air machine was one in which a confined mass of air was passed through the cycle of operations at a pressure always considerably higher than the pressure of the atmosphere. It was, therefore, what I have classified as a closed-cycle air machine. Students of heat-engine theory will recognise it as simply a Stirling air-engine working reversed; that is to say, working as a heat-pump, instead of working as a heat-engine. Kirk began by making a small model, a diagram of which is given in Fig. 15. *ABCD* was a tin plate cylinder five inches in diameter, inside of which there was a peculiar double conical plunger, *NON*, which fitted only very loosely, and could be moved easily up or down, having a stroke of 1¼ inch. The part *NN*, which goes all round, was simply a non-conducting mass. In the middle at *O* there was a regenerator which consisted of a number of plates of metallic gauze, through which, when the plunger moved, the air would pass, alternately giving up heat as it passed in one direction, and taking the heat back as it passed in the other direction. When the plunger was pushed down to its lowest point, there was scarcely any space left below it for air, consequently the air had to pass up through the regenerator into the annular space above. The substance which was to be cooled was put into the cup, *E*, and a non-conducting cover was fitted over it. A pipe, *L*, led from the bottom of the space below the plunger, and communicated with a compressing syringe or an air-pump without valves. When the piston of this syringe was pressed home it compressed the air in *ABCD*

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[1] Kelvin, "On the economy of the heating or cooling of buildings by means of currents of air." *Proc. Glas. Phil. Soc.*, Dec. 1852; *Collected Papers*, vol. i. p. 515.

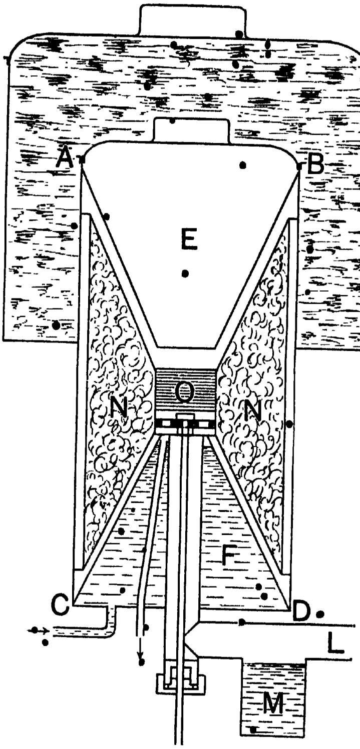

Fig. 15.

to about double its original pressure, and when it was drawn out again it allowed that air to expand, and recover its original pressure. While the air was being compressed the plunger *NON* was put up to the top, and the consequence was that the compressed air was compressed in the annular space underneath the plunger. A circulation of cold water was maintained in the conical chamber, *F*, so that the heat generated by compression was to a great extent taken up by this cold water. Then the plunger was made to descend. The air passed through the regenerator, gave up its heat to it, and came out into the upper space comparatively cool. Then, while the plunger was still down, the pump-piston was made to move out, reducing the pressure of the whole contents. Consequently, the air in this space expanded and fell much below its original temperature. Then the plunger was made to move up, and the cold air passed down through the regenerator, cooling it and taking up heat, after which the cycle was ready to be repeated. It is precisely a reversal of the cycle in the Stirling hot-air engine. With this small model, only ·5 inches in diameter, worked by hand, Kirk was able to cool air so effectively that he could freeze mercury in the cup *E*. From the model he passed to devise machines which should apply the same principle on a comparatively large scale[1]. His immediate purpose was to construct a machine for the extraction of paraffin from paraffin oil, and he carried this out successfully at the Bathgate Paraffin Oil Works. Similar machines, designed by Kirk, were employed also for ice making; one of them worked for a number of years in an ice factory at Hong Kong. It is recorded of this machine that it produced 4 lbs. of ice per lb. of coal. Let us see what this corresponds to when we express it in terms of what I have called the co-efficient of performance. We must make some assumption with regard to the number of pounds of coal which have to be burnt in the steam-engine to produce each horse-power-hour of work. It will be reasonable to assume that the steam-engine which was used to drive Kirk's machine burnt between 3 and $3\frac{1}{2}$ lbs. per horse-power-hour. In that case 4 lbs. of ice per lb. of coal corresponds in round numbers to a co-efficient of performance equal to 1. In other words, it would seem that when Kirk's machine was employed on a fairly large scale in ice-making it produced an amount of cold which was about equal to the thermal equivalent of the work spent upon it. An ideally perfect machine working between about the same limits of temperature would have a co-efficient of performance of say 10, so we see that Kirk's machine fell a long way short of the performance of an ideal machine. Nevertheless, this is probably the very best performance of any air machine of which we have a record. A machine working with air under comparatively high pressure with a closed cycle is under better conditions with regard to the co-efficient of performance than an open-cycle air-machine is, and the regenerative principle which Kirk employed had the effect of making the machine come nearer to the condition of thermodynamical perfection than is possible in the open cycle which is used in ordinary air machines. Hence this co-efficient of performance, although it is only something like one-tenth of the ideal co-efficient, is nevertheless a better performance than air machines of the more ordinary type ever reach.

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[1] **Kirk, "The Mechanical Production of Cold." *Min. Proc. Inst. C.E.* vol. xxxvii. p. 244. An appendix to this paper contains a useful bibliography relating to the early history of the mechanical production of cold.**

But why was it that Kirk's machine gave a performance so small as this? Several reasons contributed to reduce it. In all air-machines there is a fundamental difficulty, very serious in practice, in getting heat into and out of the working substance within any reasonable space of time. In this respect air machines are at a great disadvantage when compared with machines which vaporise liquid and condense vapour alternately. In the process of vaporising the liquid, and recondensing the vapour, it is much easier to effect the transfer of heat than when we are conveying heat to or from a poor conductor like air. An air machine practically requires that the working substance should, when it is at the hot end of the cycle, be carried up to a much higher temperature than the cooling water to which heat is to be rejected, and again, when it is at the cold end of the cycle that it should be carried down to a much lower temperature than the temperature of the body from which heat is to be extracted. In order that heat may flow out of the air on the one hand, and into the air on the other hand, at anything like a reasonable pace, it is necessary that the difference of temperature between the air and the substance to which it is giving heat, or the substance from which it is taking heat, should be comparatively large. Then, further, another difficulty which existed in Kirk's machine, and exists in all forms of air machines, is that they are bulky and that the loss of effect through friction in such machines is relatively very large. We must bear in mind that in all refrigerating machines whatever the frictional losses form an item of much more importance than might at first sight appear. For it is not simply that friction means the expenditure of power; but also that friction causes a development of heat within the machine itself, and that the heat so developed is for the most part taken up by the working substance. Friction not only increases the work which has to be spent in carrying the working substance through the cycle, but by communicating heat to the substance it diminishes the net or effective refrigeration which the machine produces. In any form of machine the existence of friction within the machine not only wastes power, but since the working substance has to take up the heat generated by friction it is left with less capacity for taking up heat usefully.

Kirk's machine is now obsolete, and so indeed are all forms of closed-cycle air machines. Two other inventors' names are associated with machines of this class—Allen, an American, and the German, Windhausen, who has been a pioneer in several lines of invention relating to the mechanical production of cold, notably in relation to vapour-compression machines using carbonic acid.

Open Cycle Air Machines.

We come now to the open-cycle air machines, a type which has had far more important application. This is the machine which was fore-shadowed by Lord Kelvin in 1852, and also by Professor Rankine about the same time. It was first introduced practically as a means of refrigerating by Giffard in 1873, was afterwards modified by a number of inventors, mainly English, in whose hands it attained great practical success. Mr Coleman says his attention was drawn to the subject in 1877 by Lord Kelvin, who had been consulted by Messrs Bell as to the best means of mechanically refrigerating meat during its transit over the sea, and it was in consequence of this that he devised a form of refrigerating machine which afterwards became known as the Bell-Coleman Refrigerating Machine. His type was essentially similar in general features to the machine of Giffard, which had been invented in 1873. Almost immediately afterwards the subject was taken up by Mr Lightfoot, who proceeded to develop a Giffard machine, improving it in its mechanical details, and introducing new features. About the same time also air-refrigerators were made by Mr Haslam (now Sir Alfred Haslam), who at a later date took over the manufacture of the Bell-Coleman machine, and who has probably turned out a larger number of air machines than any other engineer. Messrs Hall, of Dartford, are other makers who have contributed to the extensive use of such machines.

It was in the year 1878 that the steamer *Strathleven* was fitted with a machine of this type and made an experimental voyage to Australia, bringing home a small quantity of frozen beef and mutton as part of her cargo. This experiment led to what has now become an enormous trade.

The type of machine with which these various inventors' names are associated is in its main features substantially the same. It consists of two working cylinders, namely a compression cylinder and an expansion cylinder. The air is taken in by the compression cylinder from the room which is to be maintained at a low temperature: it is then compressed and thereby warmed: it is then cooled by circulating water while in the compressed state: it is then made very cold by expansion to atmospheric pressure, and is finally returned to the cold room from which it came.

In the diagram (Fig. 16) the space, *C*, represents a room which you may imagine is to be kept at a temperature of something like 18° Fahr. Air from it is taken in by the compression cylinder, *M*. It is then compressed from 1 to 4 atmospheres or so, and is discharged into the vessel, *A*, where it is cooled by a circulation of cold water. In the diagram the air is represented as passing into a number of pipes which are kept cool by the circulation of water outside, but in many cases the relationship is inverted, and the air passes outside the pipes, while the cold water passes through them. The air was heated in compression, but the circulating water brings it down to a temperature only a little above that of the water itself. The temperature reached

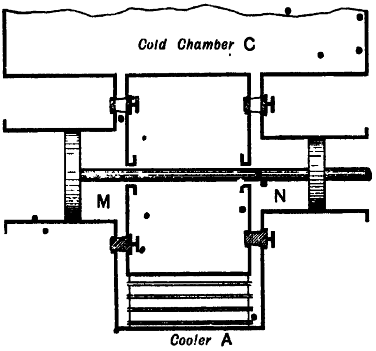

Fig. 16.

in compression is generally somewhat high. In tests of such machines it is not uncommon to find a temperature of, say, 270° Fahr. From that temperature the air is brought down to something like 60° by the cooling water, and then it passes, still under high pressure, into an expansion cylinder, *N*. It is cut off rather early in the stroke, and is allowed to expand until it falls to atmospheric pressure. It is then discharged back into the cold room. In expanding from the pressure in *A*, of, say, 4 atmospheres or so, down to 1 atmosphere, at which it is discharged, it becomes very much cooled, and reaches the cold room *C*, at a temperature of perhaps −80° or −100°, or, in some cases, even −120° Fahr. Thus the contents of the room are maintained cold by the removal of a small portion of its atmosphere by each stroke of the machine, and the restoration of that at a temperature much lower than that of the chamber itself. The expanded air requires to be considerably lower in temperature than the cold room in order that a low temperature may be maintained, in view of the fact that heat is continually leaking in from outside by conduction through the walls of the room.

Fig. 17 is an ideal indicator diagram of the cycle through which the air is taken in such a machine. The action of the compressing cylinder, *M*, is shown by the diagram *A* 1 2 *B*, and that of the expansion cylinder, *N*, by the diagram, *B* 3 4 *A*. The area, 1 2 3 4, measures the net amount of work that is expended. In this ideal diagram the compression and expansion are assumed to be adiabatic, and the volume of *A*, as well as that of *C*, is

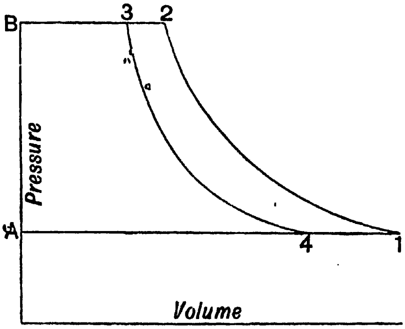

Fig. 17.

assumed to be so great that during the delivery of the air its pressure does not sensibly change. The theoretical co-efficient of performance in this cycle is much less than in the perfect cycle of Carnot. It may be expressed as $\frac{T_4}{T_3 - T_4}$ or $\frac{T_1}{T_2 - T_1}$, where the suffixes are used to distinguish the temperatures at the corresponding points, 1 2 3 4, of the diagram[1]. In practice the compression is not adiabatic: by using a water jacket or by injecting cooling water into the cylinder the compression curve may rise less steeply than the curve 1 2, which has the advantage of somewhat reducing the expenditure of work.

Practical Air Machines and their Performance.

A number of independent tests of such machines have been recorded, and from the data they furnish it appears that the co-efficient of performance ranges from something like ½ to ¾. I do not know of any authentic figures in which the co-efficient of performance is greater than ¾, and in every case it is somewhat greater than ½. Why is it so low? In the first place you observe that the actual range of temperature through which the action goes on is very large compared with the range which an ideally perfect refrigerator would employ. A machine which approached the ideal of perfection would take in its heat when the working substance was only a trifle colder than the cold chamber, and reject its heat when the working substance was only a trifle warmer than the cooling water, whereas the actual range of temperature, through which the working substance is carried in an air machine, may be from − 80° Fahr. up to 270° Fahr., when the chamber is at 20° Fahr., and the water at 60° Fahr. The widening of the range in this way is of itself a sufficient reason for a comparatively low co-efficient of performance. It is easy to show on theoretical grounds that such a machine could only be expected to have under the most favourable conditions a co-efficient of about two, and from that you must discount various other sources of loss, such as friction, and the influence of moisture.

The actual co-efficient of performance in an air machine is much less than in a machine using a vaporisable substance such as ammonia. In part this is to be ascribed to the much greater waste of power in friction, but it is largely due to the fact that with an air machine the only way of keeping the dimensions of the machine within reasonable bounds, is to chill by expansion each cubic foot of air that passes through it to a temperature very much below that of the cold chamber, and again to heat the air by compression to a temperature much above that of the cooling water. The theoretical efficiency of the Bell-Coleman cycle is lower than that of a vapour compression machine, and further, the efficiency of the vapour machine can be made in practice to approximate more closely to the theoretical value. The co-efficient of performance in practice of an ammonia machine is something like five times that of an air machine.

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[1] See Appendix B.

The influence of moisture in air machines is a point to which much attention was paid by the early workers in this field. A distinctive feature in the Bell-Coleman machine was this, that a special arrangement was employed for extracting as much as possible of the moisture from the air before it should be allowed to enter the expansion cylinder. In the early types of machines of this kind a good deal of difficulty was experienced from the formation of snow in and about the expansion cylinder and its valves. The air coming from the cold chamber is generally saturated. During compression there is no tendency to deposit moisture, for the rise in temperature more than compensates for the rise in pressure. But when the air passes into the cooler it may deposit moisture, especially if the cold chamber is not very cold. For example, air coming saturated from a room at 20° Fahr. would be nearly, but not quite, saturated after compression to four atmospheres and cooling to 60° Fahr. But if the cold room is considerably warmer than that, and the air is saturated as it leaves, moisture will separate in the cooler. In any case, even if the air leaving the cooler be not saturated, its further reduction of temperature in the expansion cylinder will tend to supersaturate it. The early inventors were so much impressed with the deposit of snow as a practical difficulty, that they not only endeavoured mechanically to remove any particles of liquid as the air left the cooler, but they used means of extracting part of the water, which was held in solution, by reducing the temperature of the air to something lower than that of the cooler itself before it was allowed to complete the cycle by expansion. Mr Lightfoot adopted the plan of dividing the whole expansion into two stages. He made the expansion compound, using a single cylinder with a piston which was made annular on one side by means of a trunk. On that side the air was expanded down to a temperature just above 32° Fahr., and on the other side its expansion was completed. In the first stage no snow was formed, since the temperature was not low enough, but water was deposited, and that was drained away before the air passed over to the other end of the cylinder. In the Bell-Coleman machine a different device was adopted with substantially the same object, namely, a series of drying pipes forming an interchanger, by which the cold air coming from the chamber was made to cool further the compressed air after it had passed through the cooler, *A*, and before it was allowed to expand. The current of air in the drying pipes was adjusted so that the temperature should fall to something near 32° in order that as much of the moisture as possible should be deposited as water (and not as snow) before the air should pass into the expansion cylinder. This device is still used by Messrs Haslam in their cold-air machines. Other manufacturers have now given up any method of specially cooling the air before expansion—that is to say, of cooling it lower than the temperature at which it naturally leaves the cooler, and they are content to effect a mechanical separation of the particles of moisture which are mixed with the air at that stage. They make no effort to extract that part of the moisture which is contained in the form of vapour in the air, and they only mechanically extract what has already been deposited in the form of water. They find that no serious difficulty is experienced from the deposit of snow during the expansion if the air is only saturated and is not charged with liquid particles before expansion begins. It is true, of course, that the deposit of snow will be somewhat greater than if an interchanger of the Bell-Coleman type be employed; but the deposit is not so great as to affect the working of the valves, and the only inconvenience appears to be that the snow-box, into which the air is discharged after expansion before it goes on to the chamber, has to be swept out oftener in one case than the other.

In the large air-compression machines made by Messrs Haslam a pair of compound steam-cylinders are placed horizontally side by side, and each is arranged in tandem with one compression and one expansion cylinder. So far as the air-cylinders are concerned, the machine is duplex, and one or both pairs may be used at pleasure. Each air-expansion cylinder has valves of the same type as those common in steam-cylinders. Meyer expansion valves are used, and are worked by prolongations of two rods which work the corresponding valves of the steam-cylinder. The compression valves consist of a group of discs placed on the cover of each compression cylinder. Large machines of this kind may be seen working in London at the Victoria Docks, each taking about 300 horse-power to drive it, causing 170,000 cubic feet of air to pass through it per hour, cooling the air to about −70° Fahr. before returning it to the cold chamber, and serving to keep cold a store of 340,000 cubic feet capacity by running in general some eight hours a day. The compression cylinder has a water jacket, so that a certain amount of the heat which is developed during compression is extracted from the air before it goes to the cooler[1]. The more heat that can be so extracted the better for the efficiency of the machine. In Mr Coleman's early machines the temperature of the air during compression was kept comparatively low by injecting water into the cylinder. This water injection is open to many practical objections, especially when sea water is concerned, and surface cooling is now exclusively used.

The large air machines of Messrs Hall are very similar in arrangement to those of Messrs Haslam. The largest is 32½ ft. long, 12 ft. wide, and 6½ ft. high, and circulates 250,000 cubic feet of air per hour. A great variety of air machines of smaller power are sold by the makers I have named, and also by Mr Lightfoot, down to belt-driven machines circulating as little as 3,000 cubic feet per hour.

Air machines have played a large part in developing the commercial applications of cold, although now the first place is

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[1] The following figures show the temperatures noted in a trial of one of these machines:

Cold Chamber	18° F.
Air entering compressor after taking up heat from the drying pipes	53° F.
After compression	291° F.
After the cooler	64° F.
After the drying pipes (on entering expansion cylinder)	46½° F.
After expansion	−72° F.
Discharge of water from cooler	65° F.

It will be seen that the actual range of temperature passed through by the working air was 363° while the difference between the temperature of the chamber and the temperature of discharge of the cooling water was only 47°.

taken by other types. When the problem is to produce a cold atmosphere in a chamber the air machine is not at the same obvious disadvantage as when we are concerned with the production of cold in a liquid. I pointed out that when air is used as a medium to extract heat from a liquid, the difficulty which is imposed by the bad conducting power of the air operates as a serious practical drawback. This objection does not apply in anything like the same degree where we are concerned with the production of a cold atmosphere. Air can be employed as a medium for cooling itself more efficiently than it can be employed as a medium for cooling anything else. Again, air machines use a working substance that is simple and harmless, and that costs nothing. When we come to deal with machines employing as working substance a liquid and vapour we find in practice very much higher co-efficients of performance than are obtained with air, and therefore better economy of power. Nevertheless, in spite of their relatively large consumption of power, air machines still do a considerable share of the refrigerating work that is done on board ship. For other uses, the air machine would not now be recommended, but for ship-board use it retains the favour of some engineers, although even there it now has two very serious competitors in the vapour-compression machines using ammonia and especially those using carbonic acid.

LECTURE III.

Absorption Machines.

We pass now to the consideration of absorption machines, which produce cold as a direct result of the ultilization of high-temperature heat, without the intermediate step of converting the heat into mechanical work. In any machine of this type there are two substances used, which have an affinity for one another so that one tends strongly to unite with or dissolve in the other when they are in the cold state, but they can be separated by applying heat. In the action of the machine they are alternately allowed to unite and made to separate. By the direct application of heat one of them is driven off in the form of a vapour. It is then condensed, in a condenser which is kept cool by circulating water to which it gives up its latent heat. This takes place at a comparatively high pressure. Then the condensed vapour is allowed to re-evaporate, and is absorbed by the other substance as soon as it does so. During this process the other substance is kept cool, consequently re-evaporation and absorption of the vapour go on at a relatively low pressure. This low pressure is associated, in the vapour, with a low temperature. While the condensed vapour is re-evaporating it takes up heat from bodies round it, and is effective for refrigeration. This completes the cycle, and the substances may again be separated by the agency of high-temperature heat, and so on.

No mechanical work need be spent in this process, and machines of this class have no co-efficient of performance in the sense in which we have used that term. In judging of their thermodynamic efficiency, what we have to compare is the refrigerating effect, or heat absorbed at the lower extreme of temperature, while the condensed vapour is re-evaporating, with the high-temperature heat which is supplied in effecting the separation of one substance from the other. Calling the refrigerating effect Q_2 and the high-temperature heat Q, as before, the efficiency of the process is measured by the heat ratio

$$\frac{Q_2}{Q}.$$

The lower extreme of temperature is determined by the pressure at which re-evaporation of the condensed vapour, and its absorption by the other substance, can be made to take place.

Of practical machines working in this general way there are two kinds. In one kind the vapour used is water, and it is absorbed by sulphuric acid. In the other kind the vapour is ammonia, and it is absorbed by water. In the first kind the action consists in driving off water vapour from a state of mixture with sulphuric acid, and then letting the acid re-absorb water vapour at a low temperature and pressure. In the second kind the action consists in driving off ammonia vapour from a state of solution in water: condensing the ammonia vapour, and then allowing it to re-evaporate and become re-absorbed by the water at a low temperature and comparatively low pressure. In both cases the absorbing substance takes the place of a pump, in maintaining a state of low pressure while the process of evaporation is going on.

Water Vapour Absorption Machines.

When water vapour is used to effect refrigeration, the pressure at which the vapour is formed, which is the pressure associated with the lower extreme of temperature, must be very low[1], and hence machines using water and sulphuric acid are often described as vacuum machines. The method of cooling by evaporating water in vacuo, and using sulphuric acid to absorb the vapour, was known almost from the beginning of the nineteenth century. Professor Leslie, in the year 1810, or thereabouts, described a laboratory experiment, in which water was frozen by placing it in a saucer under the receiver of an air pump from which the air had been exhausted, while there was under the same receiver another saucer containing sulphuric acid. After the air had been exhausted the vapour of water was given off freely, and was absorbed by the sulphuric acid, owing to its great affinity for water. The water vapour obtained its latent heat by drawing upon the stock of heat which the water contained, and the consequence was that by the time a certain portion of the water was evaporated the remainder was so much chilled as to become converted into ice. That type of machine is essentially one of the absorption type, because the active feature in it is the absorption of water vapour by sulphuric acid. The pump which produces the vacuum is an accessory and not an essential part of the machine. Actually the pump is required, because there is atmospheric air which has to be got rid of in the first place, in order to let the water vapour come into free contact with the acid. When once the air is got rid of the pump might stop acting, and the performance of the machine would continue were it not for the fact that in practice there is always a certain amount of air mixed with water in solution, which continues to be given off by the water, and so requires the action of the pump to be kept up. If we wish to convert such a machine into a continuously working one, with a complete cycle of operations, we must separate the water from the sulphuric acid in which it has been absorbed. That can be done by the agency of heat. Such a machine was, in fact, made in 1878 by Windhausen, and was practically employed on a somewhat large scale by the Aylesbury Dairy Company in the making of ice. It was described before the Society of Arts in 1882 by Dr John Hopkinson. There a complete cycle of operations was used. The water to be frozen was chilled by causing a portion of it to evaporate and be absorbed by sulphuric acid. The sulphuric acid thus diluted was passed into a vessel called the concentrator, where heat was applied to drive off the water, leaving strong acid ready to be used over again.

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[1] Water, considered as a working substance in the process of refrigeration, has the serious disadvantage that in it low temperatures are associated with very low pressures, and consequently with correspondingly large volumes.

It is interesting to notice that in this machine there was an interchanger of heat between the strong warm sulphuric acid returning to the machine after concentration, and the dilute acid on its way to the concentrator. This machine was able to freeze about 12 tons in 24 hours. A compound air-pump was used, maintaining an excellent vacuum of only one-twentieth of a pound per square inch. The ice cans in which the water was placed were, of course, air-tight, so that a vacuous atmosphere was maintained within them, and when the fresh water ran into the cans it actually froze immediately on entering by its evaporation in this vacuous atmosphere, so that when it reached the bottom of the can, it was already in a half-frozen state. The result of this was a very great rapidity of action. Six blocks of ice, weighing about 650 lbs. each, are described as having been formed in about 60 minutes after starting. Those who are familiar with the preparation of ice by modern methods are aware that, as ice is now made, it takes something like three days to produce blocks of this size.

It is characteristic of this vacuum method, where the evaporation of part of the water serves to abstract heat from the rest, that the action may easily be made rapid. This, in itself, makes the method particularly suitable in a machine of small size. Wherever you have a slow action a small machine is placed at a great disadvantage, on account of the relatively large amount of heat which leaks into it during the long time which it takes to do its work. It is highly important, in fact, in the working of a small machine, that the action should be fast, and that is, no doubt, one reason why the water-vapour absorption type of machine has survived in small sizes for domestic purposes. It is in consequence of the rapid action that this type of machine does not yield the clear blocks of ice which are obtainable by other and slower means. The bubbles of air are caught in the very act of freeing themselves from the water, and as a result the ice is white and spongy.

The vacuum is practically necessary in all such machines, in order that the operation should go on sufficiently fast. Strictly speaking, the vacuum is not an essential feature. We might have the water evaporating into air, taken up as moisture in the atmosphere within the machine, and the sulphuric acid then drying that air by absorbing the moisture from it. But such an operation would be intolerably slow, and in order that the machine should work properly it is necessary that the air be removed to let the water vapour have free access to the acid. The pump is kept working to exhaust any air which leaks in from outside, as well as the air that is gradually given off from solution in the water.

Previous to the development of Windhausen's machine Mr E. Carré, in the year 1875, introduced for domestic purposes a small form of absorption machine using water and sulphuric acid. It consists of an air-pump and a chamber to contain the acid. Connected with the handle of the air-pump is a stirring rod, which passes into the sulphuric acid chamber, so that the surface of the acid is continuously agitated in order to expose fresh surface of strong acid to contact with the vapour.

Fig. 18 shows a modified form of the small sulphuric acid absorption machine, sold by the Pulsometer Company. It has the specially effective air-pump of Mr Fleuss, shown at *A* in the figure.

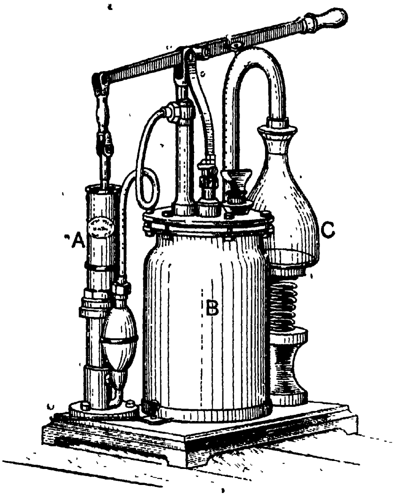

Fig. 18.

The jar *C*, containing the water to be frozen, begins to show ice on its surface in a very few minutes after we begin to work the machine. After several times of use the acid, which is kept in the container, *B*, becomes too dilute for further action, and is then replaced by a fresh supply. Its activity could of course be restored by applying heat to drive off the water it has absorbed.

Efficiency of Absorption Machines.

An important point to be noticed in regard to the efficiency of absorption machines employing two liquids is that the heat ratio must be less than unity. In other words, the heat Q_2, which is usefully extracted at a low temperature, is necessarily less than the high-temperature heat Q, which is applied at the other end of the machine. This is because a larger amount of heat is needed to evaporate one liquid when it is in a state of solution in another than is needed to evaporate it when it is in the pure state.

Take, for instance, the sulphuric acid machine and compare the low-temperature heat which is being usefully extracted by each pound of water which is evaporated, with the high-temperature heat which has to be supplied in order to re-evaporate that pound of water after it is mixed with sulphuric acid. To tear the molecules of water away from the acid involves some expenditure of energy over and above what is required to convert the water into vapour. In that part of the process which is effective for refrigeration—namely, the re-evaporation of the water—we have only to tear molecules of water from water, and the energy absorbed is consequently less. It is a familiar fact that when water is mixed with sulphuric acid a certain quantity of heat is produced. In order then to separate water from sulphuric acid, heat must be supplied, and when the water is separated in a state of vapour the whole heat required is more than the latent heat of the vapour.

There are not many tests to show what is the actual heat ratio reached in machines of this type. Dr Hopkinson, in the paper to which I have referred, says that the quantity of coal burnt in the use of the Windhausen vacuum machine was about 8 per cent. of the weight of ice produced. That may be stated as in round numbers one-twelfth of a pound of coal per lb. of ice. Now, the number of units of heat which 1 lb. of coal is capable of effectively giving out by combustion is something like 14,400. The heat taken up in the manufacture of 1 lb. of ice is 142 units so far as the conversion from water at 32° Fahr. into ice is concerned, but to that we must add the further quantity which is needed to lower the water from its original temperature down to the temperature at which it is frozen. Probably each pound of ice represents something like 200 units of effective refrigeration. In that case the heat ratio is the ratio of say 200 units usefully extracted to 1,200 units actually applied; in other words, it is a ratio of one-sixth. It will be seen later that if the same quantity of heat were applied to drive an engine of ordinary efficiency, which in its turn was set to drive a compression refrigerating machine of modern type, the refrigerating effect would be greater. High-temperature heat can be more efficiently applied to the production of cold in that way than in an absorption machine. This is true, not only of absorption machines using water vapour as the working substance, but also of those next to be described, which use ammonia vapour as the working substance, and in which water is the absorbent.

Ammonia Absorption Machines.

This other class of refrigerating absorption machine, which uses ammonia dissolved in water, is in much wider use than the sulphuric acid or "vacuum" machine. Its action is in general respects the same, but as ammonia has a much higher vapour pressure than water[1], there is no vacuum, but pressure higher than that of the atmosphere throughout the cycle. The ammonia absorption machine was invented by F. Carré about the year 1860 At first it was very crude, consisting merely of two vessels, in one of which was placed a strong solution of ammonia in water; the other in the first instance was empty, and was surrounded by cold water. The vessel containing the solution of ammonia was heated and the gas passed over under pressure into the other vessel, where it was condensed, giving up its latent heat to the water outside. A little steam passed over with it, but the main constituent of what collected in the cold vessel was liquid anhydrous ammonia. The solution of ammonia in the first vessel became more and more dilute. After this had gone on for some time, the source of heat was removed, and the vessel containing dilute solution was surrounded by cold water. The condensed ammonia in the other vessel then evaporated, being re-absorbed by the dilute solution. In re-evaporating, the ammonia exerted a refrigerating effect. By making the condenser (that is to say, the vessel which served as condenser in the first operation, and as re-evaporator in the second) with a hollow central space, in which a can of water was inserted, the re-evaporation of the ammonia was caused to freeze the contents of the can. The action in this small machine of Carré's was intermittent. It required that the vessel containing the ammonia solution should be alternately applied to the source of heat, and placed in cold water. Each of the two vessels fulfilled two separate functions; one vessel served in the first instance as the condenser of the anhydrous ammonia, then in the second instance it served as the refrigerator. Again, the other vessel served in the first instance as the generator of the anhydrous ammonia, and then in the second stage of the process it served as the absorber. Suppose, however, we have four vessels instead of two, each of the four fulfilling one function, and that we have a pump by which the liquid which has been in the absorber and has had the ammonia restored to it shall be pumped back into the generator. In that case we have the continuous machine, which was soon developed out of Carré's primitive apparatus. Several inventors contributed to the improvement—Mr Reece, Mr Stanley, Mr Mart and others adding features which are found in the ammonia absorption machine of the present day. A continuously acting machine of this class is shown diagrammatically in Fig. 19. Here we have as generator a vessel containing a solution of ammonia; heat is applied to it by means of a coil of steam-pipe within. The ammonia gas passes over from this into another vessel, the condenser, which is a coil of pipe kept cold by a circulation of cold water. There it is condensed. Then it passes through a regulating valve into another vessel, namely a coil forming the refrigerator or evaporator, as it might better be called. In evaporating there, the ammonia picks up heat from any surrounding bodies. It is evaporated under a comparatively low pressure, and consequently at a low temperature, so that if there is, say, a circulation of brine round the refrigerator or evaporator the brine may be chilled to a temperature considerably below the freezing point of water. Then the ammonia gas, having been re-evaporated, passes over into another vessel where it is absorbed by water—not by pure water, however, but by the dilute

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[1] See the tables in Appendix D.

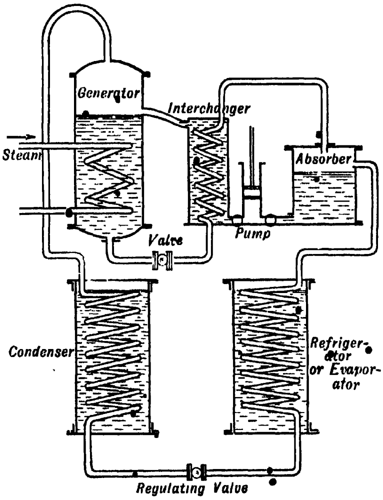

Fig. 19.

solution which is left after ammonia gas has been evaporated in the generator. In the process of generation of the ammonia gas the strong ammonia solution rises to the top on account of its smaller specific gravity, and the weaker solution falls to the bottom, from which it is allowed to pass, through a suitable check valve, into the absorber, where it meets again with the ammonia gas that has come over from the refrigerator or evaporator. After having met the gas and re-absorbed it, this liquid is pumped back to the generator where it goes in at the top. That completes the cycle of operations. In the process of absorbing the ammonia a large amount of heat is given out, and hence the absorber, as well as the condenser, requires to be surrounded by circulating water, or cooled in some other way.

Notice that as regards pressure the machine as a whole is divided into a high pressure and a low pressure part. The low pressure part consists of two organs, the evaporator and the absorber, and these are separated from the high pressure organs by the regulating valve, the check valve, and the pump.

The diagram shows between the pump and the generator another vessel, called the interchanger or economiser, which was introduced by Mart in 1870, and formed a notable improvement. In order that the absorber should act, the dilute ammonia solution in it must be comparatively cold, but that solution when it leaves the generator is hot. If it passed directly into the absorber it would have to be cooled down, and then, after the ammonia had been absorbed by it, the strong solution would have to be heated up again to the temperature of the generator. The purpose of the interchanger is to make this alternate cooling and heating of the liquid go on without much waste. The interchanger takes heat from the weak solution on its way to the absorber and gives that heat to the strong solution on its way back. Hence the strong solution reaches the generator at a temperature not very far below the temperature of the generator, and the weak solution enters the absorber at a temperature not greatly above the temperature of the absorber itself. The interchange is not complete, and, even if it were complete, the strong solution would not take up enough to raise it to the temperature of the generator, because there is a larger amount of material passing from the absorber to the generator than is passing from the generator to the absorber. Apart, however, from the loss of heat which this imperfect exchange involves, the supply of high-temperature heat to the generator must necessarily be greater than the effective refrigeration for the reason which has already been explained. In the generator we have to tear away the ammonia from the water as well as to produce the gaseous condition; whereas in the refrigerator the ammonia molecules are simply being separated from one another. Under the most favourable conditions, the heat ratio in such a machine must be considerably less than unity. It takes something like 820 or 850 thermal units to separate a pound of ammonia gas from solution with water, whereas the evaporation of a pound of ammonia gas will only take up something like 500 units, and beyond that there are several sources of loss, of which the imperfection of the exchange is one.

Fig. 20 gives an external view of an actual ammonia absorption machine as made by Messrs Pontifex and Wood, whose business is now carried on by Messrs Haslam. Such a machine has been used for many years at Meux's brewery where it

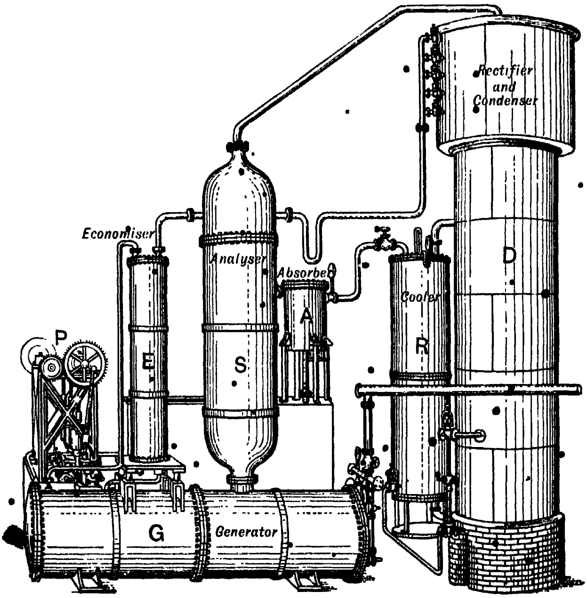

Fig. 20.

was installed in 1876[1]. The generator, *G*, consists of a cast-iron vessel with coils inside, through which steam circulates to supply heat. The vapour of ammonia when it leaves the generator is by no means in an anhydrous condition; it accordingly passes through an upright vessel, *S*, containing a series of trays, called an analyser, which separates the ammonia more perfectly from the water. Then it passes on to the uppermost coil of the condenser, *D*. This top coil is distinct from the remainder, and goes by the name of the rectifier. Its function is to purify the ammonia still further by cooling it to a temperature not low enough to liquefy the ammonia, but low enough to condense the steam which is mixed with it. The water condensed in the rectifier is caught in a series of pockets and is returned into the upper part of the analyser. The ammonia gas continues its course down through the main coils of the condenser and there becomes liquefied. It next passes through a regulating valve to the cooler or refrigerator, *R*, where it is re-evaporated and through which the brine or other substance to be covered circulates in pipes. It then goes to the absorber, *A*, where it meets with and is absorbed by a current of weak liquid from the generator, which has passed meanwhile through the economiser or interchanger, *E*. Finally, the strong solution formed in the absorber goes back to the analyser, where it drops down over a series of trays, allowing some of the gas to be extracted from it, even before it reaches the generator proper. The pump, *P*, is for pumping the strong liquid back from the absorber to the generator through the interchanger and analyser.

The absorption machine at Messrs Meux's is as large as these machines are practically made in this country. The ordinary mode of rating refrigerating machines is to state the number of tons of ice they can produce in 24 hours, whether they are actually used for the production of ice or for other purposes. This machine is employed in cooling the wort, and is rated as a 24-ton machine. It has a very good record during its long term of service, and a visit to it leaves the impression that for certain purposes there is much to be said for this comparatively simple type of machine. It cannot pretend to the same efficiency as that which is reached with a good compression machine, nor claim to be compact, but it has the advantage of few working parts, and has, apparently, very little liability to derangement. It commends itself in cases where it may be desirable to have little need of attention on the part of a skilled fitter. Machines of this class are made to a considerable extent in America. The firm of Sulzer-Vogt, for instance, supply machines having the same organic parts, but differing considerably in points of mechanical construction from the machine of Fig. 20. Their generator is a long vertical vessel, with three or more horizontal projections near the bottom of it, in which the actual generation occurs. It is not a cast-iron vessel, as in the example of Fig. 20, but is built up of wrought iron or steel plates, and the interchanger consists of two concentric pipes, the inner pipe forming one channel, and the annular space between the two forming the other. No form of heat interchanger is more effective for its purpose than that.

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[1] This machine was still employed at the date of the lecture but has now (1908) been out of use for some years.

The Sulzer-Vogt machine is used at Louisville for the working of a very interesting system of distributed refrigeration, which is also found in some other American towns. Cold is, so to speak, laid on from a central station, like gas and electricity, to the houses and shops of the consumers scattered through the town. What is actually distributed is liquid ammonia; it is sent out under pressure along mains buried in the streets, and is admitted as it is wanted to refrigerating coils on the premises of each consumer, who obtains any amount of refrigeration he pleases by regulating the amount of ammonia admitted to his evaporating coils. There are two mains, in one of which liquid ammonia is supplied under pressure, while in the other gaseous ammonia is taken back to the generating station. Each consumer's coil is simply a pipe forming what would be called in electricity a shunt between the two, and each draws off ammonia through a regulating valve to his own coil without interfering with his neighbour's. The absorption machine is claimed, I think justly, to have the advantage for such central station work, that, however fast or however slowly the ammonia vapour comes back to the central station, it can readily be taken up by absorption in water, whereas if a compression machine were used, its speed of working would have to vary in accordance with the varying demand for refrigeration. An absorption machine allows the operation at the central station to go on in a tolerably uniform way without much reference to the varying rates at which consumption occurs throughout the area of supply.

Actual Performance of an Ammonia Absorption Machine.

I pointed out that the heat ratio in all such machines is necessarily less than unity, something like 0·6 from the theoretical point of view, but you must not suppose that any actual absorption machine reaches, or nearly reaches, even this moderate figure. The most complete authentic data with which I am acquainted as to the performance of a machine of the absorption type are supplied by Professor Denton in a paper published in 1888 by the American Society of Civil Engineers. He tested a refrigerating machine of the Pontifex type, employed to cool brine from 21° Fahr. to 16° Fahr., and supplied with cooling water at 54½° Fahr. He found that each pound of steam supplied to the machine gave up 932 thermal units, and effected an amount of refrigeration measured by 243 thermal units; in other words, the heat ratio—namely, the ratio of the effective refrigeration to the heat supplied—was $\frac{243}{932}$ or 0·26. In round numbers, this machine did an amount of refrigeration equal to one-quarter of the heat which was supplied to it in the steam. The steam which was reckoned in this test included not only the steam supplied to the generator, but also that required to drive the pump. It is interesting to compare this figure with the theoretical efficiency of an ideally perfect refrigerating machine. Taking the limits of temperature which were used in Professor Denton's test, namely 272° Fahr. and 16° Fahr. for the two extremes, and 67° Fahr. (a mean of 54½° and 80°) for the middle temperature, an ideally perfect machine made up of a combination of reversible heat-engine with reversible heat-pump would give a heat ratio of 2·61 instead of 0·26. This shows how far the ammonia absorption machine falls short of being reversible in the thermodynamic sense. It only gets about one-tenth of the refrigerating effect that might, in theory, be got from the same quantity of high-temperature heat if that were applied to produce refrigeration in the ideally most efficient manner.

[Note added 1919. In an ammonia absorption process patented by Mr W. W. Seay the gas is absorbed by a dry salt of ammonium such as the nitrate or the thiocyanate. The gas and salt on uniting form a liquid from which the gas is again distilled off by heat. No water is used. This cycle is efficient, for a quantity of heat less than the latent heat of the gas serves to separate the gas from the salt, because the salt becomes a solid as the gas leaves it, and gives out heat in solidifying.]

LECTURE IV.

The Vapour Compression Process.

I PASS on to speak in some detail about the process of refrigeration which is now far and away the most important process of all —the vapour compression process. Air-machines and ammonia absorption machines find a limited amount of use; but the great bulk of the work of refrigeration is done by machines which act by the mechanical compression of a condensible vapour. The scientific and historical interest of other methods have led us to spend a considerable time upon them, but in point of commercial importance they take a very secondary place. Moreover, the vapour compression process is the most efficient of all. It allows a co-efficient of performance to be reached in practice which makes a very respectable approach to the thermodynamic ideal.

I explained in the first lecture, in speaking of Fig. 8, how a liquid with its vapour could be carried through a perfect refrigerating cycle, forming a reversal in all respects of the cycle of Carnot. This would necessitate the use of an expansion cylinder as well as a compression cylinder, the function of the expansion cylinder being to allow the liquid from the condenser to cool itself adiabatically to the temperature of the refrigerator. In practice the expansion cylinder would be very small—much smaller in comparison with the compression cylinder than appears from Fig. 8, for that diagram was drawn to represent a machine using air. Expansion would take place from the volume of the liquid up to a volume in which enough of the liquid is evaporated to reduce the temperature of what is left down to the temperature of the refrigerator. That is generally quite a small proportion of the whole—something like one-tenth or, at the most, one-quarter—and therefore quite a small expansion cylinder would suffice. But in all actual machines which employ a vapour the expansion cylinder is omitted altogether and the organs are those shown diagrammatically in Fig. 21. There the vapour from the refrigerator, *C*, is compressed in the compressor cylinder *B* into the condenser, *A*, where it is liquefied; but it returns from *A* to *C* through a simple regulating throttle-valve instead of through an expansion cylinder. In passing through the throttle-valve part of it becomes gaseous, so that when it reaches *C* it consists of a mixture of liquid and vapour, but the liquid part preponderates. It continues to evaporate in *C*, and, in doing so, takes up heat from the surrounding brine or whatever is there to be cooled.

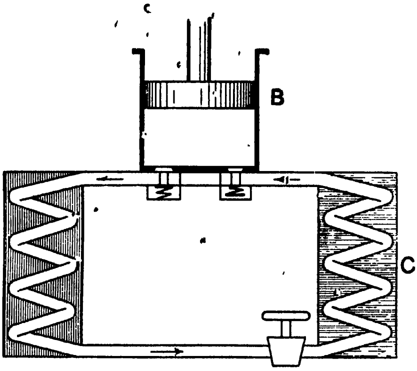

Fig. 21.

Any liquid which can be alternately liquefied and vaporized, or, in other words, any liquid whatsoever would serve as a possible working substance in such machines. Liquids which have been used are water, sulphuric ether, sulphurous acid, ammonia, and carbonic acid. A machine employing water for its working substance in this way must be a vacuum machine on account of the low vapour pressure of water, but its action is, of course, different from that of the sulphuric acid vacuum machine already described. Here the working substance undergoes no solution nor chemical change. The vapour as it is formed is disposed of by the compressor cylinder's action as a pump instead of by absorption in acid. Windhausen's machine, to which I have referred, was sometimes used without the sulphuric acid, and in that case it formed an example of the class of machines we are now dealing with. There was only this difference, that the water vapour discharged by the air-pump did not complete a cycle by returning to the refrigerator, but other water took its place. Another machine of the same class was put on the market some years ago by Messrs Southby and Blyth, where water was the working substance, and a vacuum was maintained by pumping without the use of sulphuric acid. The enormous volume of the vapour which has to pass through the pump in such machines is a serious practical objection to their use. It makes the machine bulky and the frictional losses relatively large. It may occur to you that there is another disadvantage in the use of water—namely, that if we attempt to evaporate water at a temperature below 32° Fahr. it will freeze. That, however, can be got over when lower temperatures are wanted by using brine instead of water for the working substance. The working cycle remains practically the same, and the lower limit of temperature may then be much reduced. But the vapour becomes bulkier than ever the lower you go in temperature; the machine is inconvenient and mechanically inefficient. The work spent in overcoming the friction of the piston packing tends to form a large part of the whole work that has to be expended. Remember that any heat developed in the compressor by mechanical friction not only adds to the amount of work to be done in driving the machine, but takes away from the effective refrigeration which the substance should produce.

Choice of a Liquid in Vapour Compression Machines.

In the choice of a liquid for use as working substance in a compression machine there are several points to consider—some thermodynamical and some of a general practical kind. One of the first is the question of bulk of which we have just been speaking, and the consideration of it may be said to put water at once out of court. The volume of 1 lb. of water vapour at 32° Fahr. is 3,416 cubic feet. Its latent heat is 1,092 thermal units. Hence the piston of a machine using water would have to sweep through something more than three cubic feet for each thermal unit of refrigeration, if the temperature of refrigeration were 32° Fahr. and still more if the temperature were lower. Compare this with the volume to be swept through when ammonia is used. Ammonia vapour at 32° Fahr. occupies about 4·8 cubic feet per lb., and its latent heat is 568 thermal units; hence the piston would in that case have to sweep through considerably less than one-hundredth of a cubic foot for each unit of refrigeration. With sulphurous acid for working substance the piston would have to sweep through about one-fiftieth of a cubic foot, and with carbonic acid barely one five-hundredth. In comparison with any of these the bulk of the water-vapour machine is excessive[1].

Another question to consider is, what will be the working pressure on the two sides of the machine—the high-pressure side, *A*, and the low-pressure side, *C*. These pressures are determined by the temperatures of the condenser and refrigerator respectively. Their limits are fixed for any given vapour used as working substance when we are told what is the temperature of the water into which heat is rejected and what is the temperature at which refrigeration is to be performed. In the choice of a working substance one has to ask whether the pressures corresponding to these limits are either inconveniently high or inconveniently low. With water, they are excessively low; the vapour pressure of water is considerably less than one pound on the square inch even at the highest temperature likely to be reached on the warm side of a refrigerating machine. Sulphuric ether was at one time in favour as a working substance, but its vapour pressure is only 3·54lbs. per square inch at 32° Fahr. and is below the pressure of the atmosphere for all temperatures under 95° Fahr. Hence, in an ether machine both the high and the low pressure sides would be at less than atmospheric pressure, and any want of tightness would mean a leakage of air into the machine, not a leakage of ether out. This is a serious practical disadvantage, for the presence of air reduces the efficiency of the process. Besides, these ether machines were bulky, and the use of an inflammable vapour was objectionable. Modern machines use one or other of three substances, sulphurous acid, ammonia, and carbonic acid.

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[1] The following are the figures for the four substances named, at a temperature of 32° Fahr.

	Pressure in lbs. per sq inch	Vol in cubic feet per lb	Vol per 1000 units of net refrigerating effect (approx.)
Water	0·085	3416	3200
Sulphurous Acid ...	22·5	3·4	22
Ammonia	61·8	4·8	9
Carbonic Acid	535	0·17	2

If we take a temperature of −4° Fahr. as a lower limit, that being about the lowest temperature at which refrigeration is practically performed, we find that the (absolute) pressure of the vapour in these three substances is for sulphurous acid about 9 lbs. per square inch, for ammonia about 21 lbs. per square inch, and for carbonic acid about 289 lbs. per square inch. If, again, we take 86° Fahr. as a representative upper limit at which heat is liable to be rejected (though sometimes, as, for instance, in the tropics, we may have to deal with a somewhat higher temperature) we find that sulphurous acid has a pressure of 66 lbs. per square inch, ammonia of 171 lbs. per square inch, and carbonic acid a pressure of 1,039 lbs. per square inch. On the diagram (Fig. 22) curves are

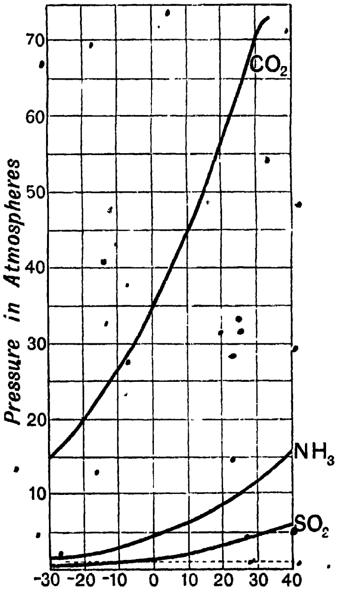

Fig. 22. Vapour Pressures in Carbonic Acid, Ammonia, and Sulphurous Acid.

drawn to show the vapour pressures of these substances in relation to the temperature[1]. There the scale of temperature is given in Centigrade degrees, and the pressures are expressed, not in lbs. per square inch, but in atmospheres, each atmosphere being about 14·7 lbs. per square inch. You observe, then, that within the practical limits which I have just indicated the pressures of ammonia range from something like 20 lbs. to something like 170 lbs. on the square inch. These are just such pressures as engineers are accustomed to deal with in ordinary steam-engine work; they are pressures which present no serious difficulty as regards the keeping of joints and glands tight. With sulphurous acid the pressure is lower, and it falls below the pressure of the atmosphere when the temperature is anything under 14° Fahr. This exposes the low temperature side of the machine to the risk of air leaking in, which is then particularly objectionable, because it might produce sulphuric acid and corrode the metal.

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[1] For numerical values see the tables in Appendix D.

In vapour compression machines of any class leakage of the working substance out to the atmosphere is in general attended by no more serious disadvantage than that a portion of the charge is thereby lost, and has to be renewed from time to time, whereas leakage of the atmosphere into the machine means a diminution of the efficiency of the process, and in some cases it also means that chemical action is liable to go on between the working vapour and the oxygen of the air. In some cases however, as on board ship, leaking of the working substance outwards may be attended by serious practical inconvenience and even danger, on account of the confined nature of the space into which it leaks.

With carbonic acid, which is the third substance on our list, the pressures are greatly higher than in either of the other two. The volumes are correspondingly small, so that machines using carbonic acid have the advantage of great compactness in their working parts. But the keeping of joints and glands tight is a very much more serious mechanical problem in these machines, and even with the best construction and most careful use the loss of the working substance is in general greater in them than in others. On the whole, taking pressures as well as volumes into account, ammonia has the advantage over either of the other substances as regards the convenience of its pressure and volume range. The pressures that have to be dealt with are neither excessively high nor excessively low; and the bulk of an ammonia machine is moderate.

Other points to be considered are the cheapness and stability of the working substance, cheapness in regard to replacement as well as first cost, and stability in the sense of not being liable to chemical change through lapse of time, or through repeated passage round and round the cycle of operations. Again, the working substance must not exert chemical action on the metal of the machine. Carbonic acid is without action on brass or copper as well as iron. Whereas ammonia, though without action on iron, is an active solvent of brass and copper, and these metals must, therefore, be entirely excluded from the machine and the coils and all the parts of the working system when ammonia forms the working substance.

Again, we must always reckon on the possibility of leakage, though the probability is less with some substances than with others on account of differences in pressure; and it is important to enquire how far the working substance, should it leak, will be innocuous—how far it may be allowed to escape into a closed space without producing serious consequences. In this particular, when the machine has to be put in a confined space on board ship carbonic acid is rightly regarded as less objectionable than ammonia. Another point is the facility which the substance offers for the detection of leaks, should they occur. In this respect both of the other two substances have the advantage over carbonic acid, because of their smell. These are practical considerations, and the amount of weight to be given to any one of them will depend on the circumstances of the particular case.

Comparison of the Substances as to Thermodynamic Efficiency.

But, in dealing with the relative merits of the various materials, there is still one important element which concerns the thermodynamics of the subject. It has to do with the question—How far is one liquid more able than another to approach the thermodynamic ideal of efficiency? If we were dealing with the Carnot cycle of operations, it would be a matter of complete indifference which of the various liquids we employed, so far as thermodynamic considerations went, because in that case the efficiency would depend only on the limits of temperature, and would be unaffected by the properties of any particular working substance. But the case is different with the cycle which is actually used. That cycle differs from the Carnot cycle in the omission of adiabatic expansion and in the substitution of the regulator or throttle-valve, through which the liquid is allowed to stream, for the expansion cylinder. Consequently, not only do we lose some work which might be saved (namely the work done in the expansion cylinder), but the equivalent of this work is carried on into the evaporator in the form of heat, in the liquid which streams through the regulating valve, and this reduces the useful refrigerating effect. The liquid is coming from a vessel at a relatively high temperature into a cold vessel, and brings with it a quantity of heat which is equal to the difference in temperature between the two multiplied by the specific heat of the liquid. In the evaporator it takes up effectively a quantity of heat which depends upon the latent heat of the vapour. Hence the amount of the loss which results from omission of the expansion cylinder depends primarily upon the proportion between the specific heat and the latent heat of the working substance.

To express this in figures, let r be the latent heat of the vapour, and let q_1 and q_2 be the amounts of heat contained in the liquid at the respective temperatures T_1 of the condenser and T_2 of the evaporator or refrigerator. The heat which the liquid carries over is $q_1 - q_2$, and this reduces the refrigerating effect from r to $r - (q_1 - q_2)$, assuming the evaporation in the refrigerator to be complete[1]. The quantity $q_1 - q_2$ is equal to the specific heat of the liquid[2], multiplied by the difference of temperatures, $T_1 - T_2$. If we assume, as an example, that T_1 is 62° Fahr., and T_2 is 32° Fahr., the numbers for the various substances are as follows:—

—	Latent heat, r	Liquid heat $q_1 - q_2$	Refrigerating effect $r - (q_1 - q_2)$	Proportion of loss, namely, $\frac{q_1 - q_2}{r}$
Water...............	1,092	30	1,062	$\frac{1}{36}$
Sulphurous acid ...	164	10	154	$\frac{1}{16}$
Ammonia	568	27	541	$\frac{1}{21}$
Carbonic acid	100	16	84	$\frac{1}{6}$

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[1] There is a small further reduction due to the work which the pressure of the liquid does in forcing the liquid through the throttle-valve (see footnote on p. 70).

[2] The specific heats of the four substances in the liquid state are approximately:

Water ...	1
Sulphurous Acid	0·32
Ammonia ...	0·9
Carbonic Acid	0·54

Or take a case where the range of temperature is wider, and let T_1 be 68° Fahr., and T_2 be 14° Fahr.: a similar calculation then shows that the loss due to the heat brought over in the liquid amounts with ammonia to 8½ per cent. of the gross refrigeration r, with sulphurous acid to 10½ per cent, and with carbonic acid to 29 per cent. With water the loss amounts to barely 5 per cent., but water, though best in this respect, is out of court for the reasons already given. Of the other substances, ammonia comes in this respect at the top of the list; and carbonic acid makes a bad third.

In other words, of the three substances ammonia gives us the least falling away from the ideal cycle of Carnot, and carbonic acid gives a relatively large falling away from that ideal.

Entropy Diagrams for Vapour Compression Machines.

The working of machines of this class is most thoroughly grasped by the aid of the entropy diagram. Consider what is the form that this diagram will take for the working of a vapour compression machine. The entropy diagram is familiar to many persons in relation to the steam-engine, where we have an almost precisely reversed set of operations from those which we are now dealing (Fig. 23). It may be useful to refer for a moment to the

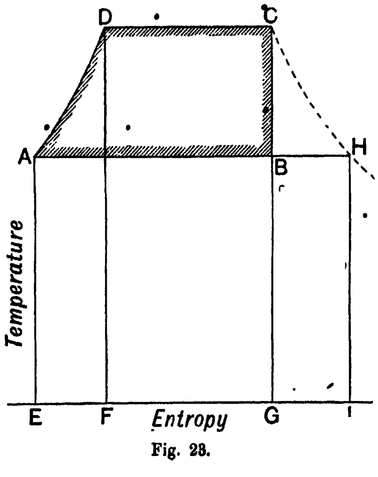

Fig. 23.

steam-engine cycle of operations before coming to the refrigerating cycle. In it we begin with the water delivered by the feed-pump to the boiler at the temperature of the feed, which is the lower limit of temperature. While the feed-water is being raised to the temperature of the boiler it is taking in heat, and this part of the operation is exhibited on the entropy diagram by a line that slopes upward, *AD*. The point *A* is plotted at a height above the datum line corresponding to the absolute temperature of the feed. The actual entropy of the water in this state is a matter with which we need not concern ourselves: we have only to do with changes of entropy reckoned with respect to this state as a convenient starting point. From *A* to *D*, which represents the process of heating the feed-water up to boiler temperature, heat is being taken in and the entropy is accordingly increasing. This increase is represented, on the scale used to represent changes of entropy, by the distance *EF*. *D* is accordingly placed to the right of *A* by the distance *EF* and at a height which corresponds to the absolute temperature in the boiler. The heat and entropy are reckoned, and represented in the diagram, per unit quantity of the working substance.

Remember that in the entropy diagram the heat taken in during any operation is represented by the area under the line which represents that operation. The heat taken in by the feed-water of the steam-engine while it is rising from the temperature of the feed to the temperature of the boiler is represented by the area *EADF*. The next part of the operation is the conversion of the water into steam in the boiler. This is represented by the line *DC*, and the heat taken in during that process is *FDCG*. *FG* is the gain in entropy which occurs during the process. The substance is at that time taking in heat without change of temperature; and hence the entropy line *DC* is parallel to the base. If we were to suppose a number of different temperatures at which evaporation might occur, and were to draw the corresponding line to *DC* for each of them, we should get a boundary line (passing through the extremities of all) of the kind represented by the dotted line *CH*. It is convenient to have this line sketched on the diagram. It represents the values of the entropy of saturated steam at various pressures and temperatures. After the operation *DC* the next step is the expansion of the steam in the cylinder, and if we suppose the cylinder to be a non-conductor, so that the expansion is performed adiabatically, we have the line CB to represent this process, no heat being given out or taken in. In this process there is no change of entropy but the temperature falls. Suppose the expansion to be continued until the steam falls to the temperature of the condenser. Part of the steam, namely, the fraction $\frac{BH}{AH}$ has become condensed during the expansion. The remainder is now condensed, this operation being represented by the line BA. In being condensed it gives out an amount of heat represented by the area $GBAE$[1].

Here we have the same cycle of operations as we have in the refrigerating machine, only performed the other way about. Trace the cycle in the order $CDABC$, and it then represents the refrigerating process. The operation CD is the condensation of the compressed vapour. DA is the cooling of the condensed liquid as it passes into the refrigerator. AB is its evaporation there, and BC is the compression. Observe that if the vapour is only to be saturated, and not superheated, at the end of the compression, compression must begin at B and not at a point further out along the line BH. That is to say, the evaporation AB must be incomplete, leaving the fraction $\frac{BH}{AH}$ still unevaporated and mixed as liquid with the vapour when it enters the compression cylinder. In other words the evaporator or refrigerator must *prime* to that extent if this vapour is not to become superheated when it is compressed. In many cases superheating does take place, but it is only when the proportion of liquid to vapour in the mixture admitted to the cylinder is in the proportion of BH to AB that an adiabatic process of compression will have the effect of bringing the whole into the condition of saturated and dry vapour when it leaves the compression cylinder. The next process CD is performed in the condenser, and is the process with which we supposed the cycle to begin.

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[1] If all the substance were in the state of saturated vapour when the process of condensation begins, the process would start from H and the heat given out would be the area under AH, namely $AEHI$. At B, however, we have a wet mixture, and as the heat given out is the area under AB, namely $EABG$, it follows that at B the fraction $\frac{AB}{AH}$ is the fraction remaining to be condensed. In other words in the mixture at B the fraction $\frac{AB}{AH}$ is vapour and $\frac{BH}{AH}$ is liquid.

The area $AEFD$ is the heat which is carried over by the liquid into the evaporator in consequence of the absence of an expansion cylinder; the net amount of refrigeration is the area $ABGE$ *minus* the area $AEFD$. The question of efficiency as affected by the physical differences between any one working substance and another depends upon what relation the area $AEFD$ bears to the area $AEGB$—that is to say, on the relation of $q_1 - q_2$ to xr, where x expresses the fraction which is vaporised before compression begins, or $\frac{AB}{AH}$. The area of the closed figure $ABCD$ measures the work that has to be expended in performing the cycle[1].

Draw a line KL (Fig. 24) so that the area $EALK$ is equal

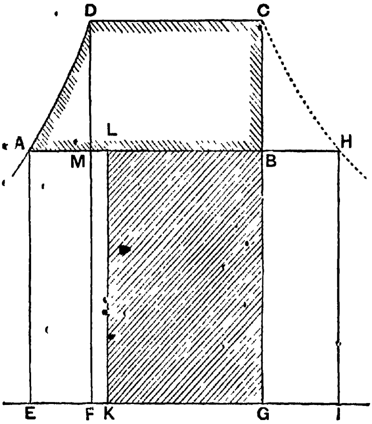

Fig. 24.

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[1] The refrigeration cycle is not strictly a reversal of the steam-engine cycle, because the streaming of liquid through the regulating valve is not a reversal of the action of a feed-pump. To make the one a strict reversal of the other would require what we may call a negative feed-pump in the refrigerating machine—that is to say, a working cylinder which would get out of the liquid the equivalent of the work spent on the feed-pump. The work in question is $v'(p_1 - p_2)$, where v' is the volume of the liquid, and p_1 and p_2 are the pressures in the vessels A and C respectively. Hence the work which must be spent on the refrigerating machine with a throttle valve is really greater than the area $ABCD$ by the amount $v'(p_1 - p_2)$; and the net refrigerating effect is less by the same amount, being $xr - (q_1 - q_2) - v'(p_1 - p_2)$. But the term $v'(p_1 - p_2)$ is so small except in the case of carbonic acid that in most calculations it may be omitted without serious error. It is taken account of in the figures for carbonic acid given on p. 76.

to the area *EADF*, or, in other words, so that *FMLK* is equal to *AMD*, then the cross-hatched area *KLBG* measures the net refrigerating effect per unit quantity of working substance put through the cycle. The co-efficient of performance is the ratio of the area *KLBG* to the area *ADCB*, which is the work done by the compressor.

In Fig. 25 there are drawn to one scale the entropy temperature charts of ammonia, sulphurous acid, and carbonic acid. On the left in each diagram is the line taken by the substance in changing its temperature without being vaporised. On the right of each is a line corresponding to the dotted line *CH* of Fig. 23, showing the values of the entropy when the substance is completely vaporised at various temperatures. These figures bear out the conclusion come to before, that the absence of the expansion cylinder causes least loss of effect in ammonia and most in carbonic acid. In each case we have to distinguish between what may be called the gross refrigeration due to the evaporation of the liquid and the net refrigeration, which is that quantity minus the area under the sloping line on the left-hand side. In the ammonia diagram the lines are as nearly as possible straight lines, and in the sulphurous acid diagram they are very nearly straight for this range of temperature. The carbonic acid diagram has a rounded top at the critical temperature of the gas. The charts

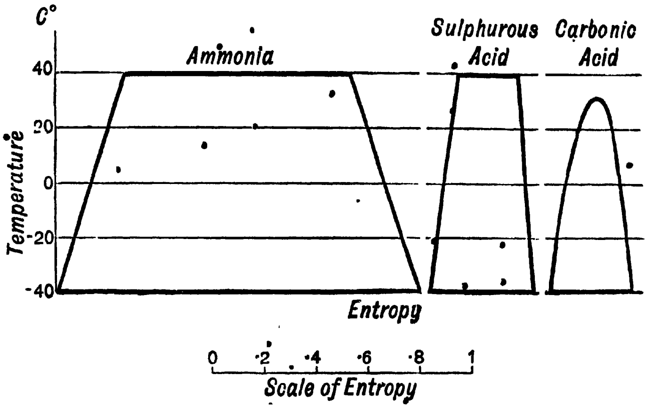

Fig. 25.

for ammonia and sulphurous acid are sketched here for temperatures ranging up to 40° C. only. If they were continued to sufficiently high temperatures the sloping lines on the right and left in each case would meet in a rounded curve, the top of which correspond to the critical temperature. We shall call the curve of which both these lines are parts the "boundary curve."

Wet and Dry Compression.

" When compression is carried on in such a way that the vapour does not become superheated it is technically called wet compression. When wet compression is used the regulating valve is adjusted so that the compressor sucks in a mixture of vapour and liquid, with the result that the gas is still saturated at the end of the compression. By closing the regulating valve a little the vapour passing over from the refrigerator may be made to contain less liquid mixed with it, and if it contains none the compression is said to be dry. In dry or partly dry compression the vapour becomes more or less superheated. An entropy diagram for ammonia using dry compression is sketched to scale in Fig. 26. Refrigeration is there supposed to take place at -10°C., and condensation at 20°C. The line CK shows, in a general way, how the entropy of the ammonia gas changes when it is superheated under constant pressure, starting from the saturated condition at C. The point K is determined by the intersection of this line by the vertical line HK through H, which represents adiabatic compression. It is supposed here that the compression

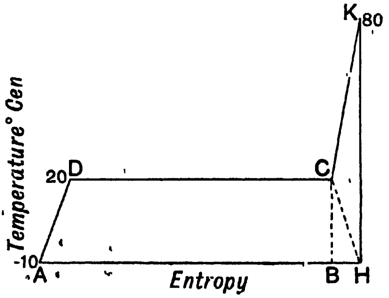

Fig. 26. Ammonia Cycle with Dry Compression.

is perfectly dry; in other words, that the compressor takes in only dry vapour. The line representing the compression process in the diagram accordingly starts from H, which corresponds to a state of complete vaporisation of the substance. Then AH represents the evaporation in the refrigerator, HK the compression, KC the cooling of the compressed gas from its superheated state to the temperature of the condenser, CD its condensation in the condenser, and DA the cooling of the condensed liquid as it passes over into the refrigerator. During compression the temperature rises in this example to about 80°C. This superheating enlarges the area of the diagram, and therefore increases the amount of work to be spent in working the machine. On the other hand, the refrigeration is now greater by the amount of the area under BH—measured down to the base line which would correspond to the absolute zero of temperature.

Compression starting from H may be described as completely dry. At H the vapour is just saturated, and as soon as compression begins it becomes superheated, the amount of superheat increasing as compression continues till the extreme amount is reached at K.

On the other hand if compression starts from B there is no superheat at any stage. The substance is wet to begin with and remains wet until just the end when (at C) it reaches the dry but still saturated state.

Between these two extremes we have any number of intermediate varieties, for if compression starts at any intermediate point between B and H the substance will at first be wet, and will remain wet until the vertical line crosses CH, after which superheating will begin, and the final degree of superheat will be determined by the point at which the vertical line meets the line CK.

An interesting question follows—how far does the wetness or dryness of the compression affect the efficiency of the process, how far does it affect the ratio between the heat taken up in the refrigerator and the work done on the machine? Knowing the form of the lines in the entropy diagram, it is easy to calculate how much the ideal performance will be affected if we change from wet compression to dry, or to an intermediate kind, such as would be got by beginning to compress at some point between B and H. If you make this calculation, you will find, in the case of ammonia, that it makes no very substantial difference to the theoretical co-efficient of performance whether you make the compression wet or quite dry, or anything between the two. With the same temperatures of condenser and refrigerator as those in Fig. 26 (20° C. and – 10° C.), I find that the dry process with the compression line *HK* makes the co-efficient of performance 8 per cent. less than the wet process with the compression line *BC*. This comparatively small difference may seem surprising in view of the augmented range of temperature through which the substance is carried—its upper limit is now 80° C. But it must be borne in mind that the great bulk of the heat is still rejected during the condensation at 20° C., only a small quantity being taken from the gas at higher temperatures in cooling it down to the temperature at which condensation occurs. If you take a compromise mode of working, where there is a smaller amount of superheating, the effect on the performance is of course less. If, for example, compression begins midway between *B* and *H*, so that the amount of superheating is about half of that indicated in the diagram, say 30° C., the co-efficient of performance is only about 2 per cent. less than it is in the wet process, and if there were 15° C. of superheating, the reduction is barely one-half per cent. The moral of this is that so far as thermodynamic theory goes there is exceedingly little to choose between the perfectly wet process as it is approximately performed, for instance, in the Linde machine, and the more or less dry processes used by some other makers. I would emphasise this because claims of an extravagant kind are sometimes made in favour of one process or another in this respect. So far as thermodynamic theory is concerned there is little difference in the efficiencies of the wet and dry modes of compressing in ammonia machines. What little difference there is in this regard is in favour of the wet process as compared with any process involving considerable superheating. Strictly speaking, a very small amount of superheating is probably advantageous as compared with the absolutely wet process. It is only when we come to a distinctly high superheating that there is any material falling off in the co-efficient of performance. All these remarks, however, require this qualification, that in a real machine the process of compression is never adiabatic.

These calculations assume an adiabatic process, but in real cylinders there is always a give and take of heat between the working substance and the metal. It is by no means easy to say precisely how that affects the efficiency of the process. The exchanges of heat between the vapour and the cylinder will have the general effect of lessening the co-efficient of performance, and with dry gas the exchanges of heat will be less than they are with wet gas. Hence it is probable, on general grounds, that the loss of efficiency which such exchanges cause will be reduced somewhat by allowing a small amount of superheating, and Professor Schröter tells me that he has experimental evidence bearing out that conclusion. At most, however, we cannot expect much difference in efficiency between the wet process and one carried out in such a way as to produce some superheating, so far as ammonia is concerned. With carbonic acid, when the upper limit of temperature approaches the critical point, superheating is decidedly advantageous, and even necessary.

It may be added that, in general, a little superheat at the end of compression is practically useful as giving evidence that the regulating valve is not being kept too widely open. In other words it is a guarantee that we are beginning the process of compression without any excessive amount of wetness. To start compressing from a point to the left of *B* would result in having the vapour still wet at the end of compression, and would reduce the refrigerating effect without any compensating advantage. [It may be added that since these lectures were delivered the tendency in practice is to prefer dry compression.]

Calculated Theoretical Performance.

By help of the entropy diagram, or otherwise, we may estimate the theoretical performance in a cycle using wet compression, and compare it with the limiting performance in the perfect Carnot cycle[1].

I have worked out the figures approximately for ammonia and for carbonic acid, assuming the upper limit of temperature to be 20°C. or 68° Fahr., and taking various lower limits, ranging from 10°C. to −20°C. The results are given in the Table below, along with the ideal co-efficient of performance in a perfect machine, which is added for the sake of comparison.

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[1] This is most conveniently done, in the case of carbonic acid, by means of the ϕI diagram described in the Appendix.

Theoretical co-efficients of performance in vapour compression machines, using wet compression, the upper limit of temperature being 20° C., the compression being treated as adiabatic.

Lower Limit of Temperature. Deg. C.	Theoretical Co-efficient of Performance		Co-efficient of Performance in Carnot Cycle
	Ammonia	Carbonic Acid	
10°	27·8	21·1	28·3
5°	18·1	13·0	18·5
0°	13·2	9·3	13·6
− 5°	10·2	7·0	10·7
− 10°	8·3	5·6	8·8
− 20°	5·9	3·8	6·3

The curves of Fig. 27 exhibit these results. It will be noticed that with ammonia the ideal performance here considered, namely, that of a compression machine without an expansion cylinder, is only a little less than the "perfect" ideal performance which would be obtained by following Carnot's cycle. Hence with this substance

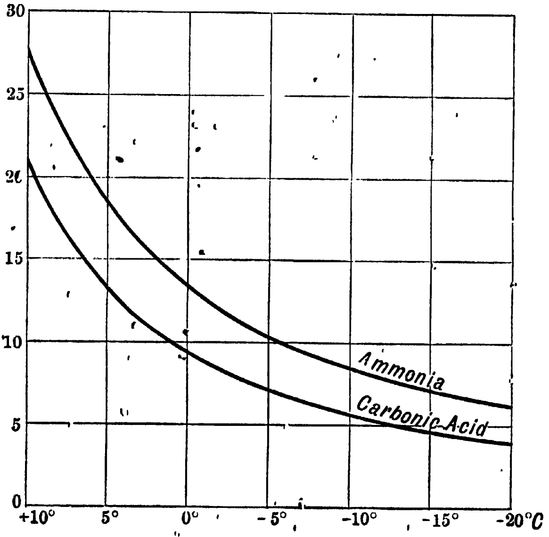

Fig. 27. Ideal Performance in Vapour Compression Machines without an Expansion Cylinder.

we should gain almost nothing by adding an expansion cylinder to the machine, nothing, certainly, that would in any way compensate for the increase of complexity and cost, and the loss of power and of refrigerating effect through friction, which an expansion cylinder would involve.

With carbonic acid there is considerably more falling away from the ideal of Carnot, mainly for the reason which I have already explained, that the specific heat of the liquid bears a greater proportion to the latent heat of the vapour, and also because the volume of the liquid is relatively considerable. But even then the saving in work which an expansion cylinder would bring about is not great, and in practice we never find the expansion cylinder, even in carbonic acid machines.

These results apply to wet compression. We shall see presently that with wet compression carbonic acid is at a serious disadvantage, which is considerably reduced by making the compression dry, or nearly dry.

Both substances would give results falling more considerably short of the Carnot ideal if the upper limit of temperature were raised. This is notably true of carbonic acid. Say, for instance, that we have to deal with machines used on a voyage through the tropics. The condensing water may have a temperature of 90° Fahr. (32° C.), or even more. In that case not only would the Carnot ideal co-efficient be lower, but both machines would fall more short of it. The carbonic acid machine would fall in efficiency much more than the other when such a temperature is approached, for carbonic acid is then in the neighbourhood of its critical point, but with dry compression it would recover a fair degree of efficiency.

Carbonic Acid and the Critical Point.

The critical point is the temperature above which the substance cannot be made to change from a gaseous to a liquid condition. In the entropy chart it is the temperature at which the boundary lines on the right and left meet if you extend them upwards. In any substance these lines are converging towards one another as the temperature is raised. Go on raising it, and you find that they bend towards one another, and finally meet in a continuous curve, giving the diagram a rounded top. This appears in the carbonic acid diagram in Fig. 25. At any temperature below the critical point there is a well-defined change of state between the liquid and the vapour, a change which is associated with the taking in of heat without change of temperature, but when the critical point is reached there is no such change. With ammonia or with sulphurous acid the critical temperature is so high that no account has to be taken of it in calculation relating to refrigerating machines which use these substances. But in the case of carbonic acid the critical point is comparatively low; it comes at a temperature about 31° C. or 88° Fahr., so that it comes within the range of temperatures that might have to be used in a machine working in a tropical climate. The effect of approaching the critical point is to increase what we have called the liquid heat, namely, the heat that passes over in the liquid from the condenser to the refrigerator, in comparison with the latent heat that is taken up by evaporation in the refrigerator, and, consequently, to augment the loss which results from the absence of an expansion cylinder. The performance of carbonic acid falls off very materially when the condensing water is so warm as to approach this critical temperature, but the machine does not by any means cease to act as a refrigerator, even when the critical temperature is surpassed. It has been suggested that this might happen, but by arranging matters so that the gas is superheated during compression a respectable co-efficient of performance is maintained.

Thanks to the investigations of Dr Mollier it is not difficult to estimate with precision what the theoretical performance of a carbonic acid machine will be under any particular conditions of temperature, and with any assumed degree of dryness in the vapour at the beginning of compression[1].

Basing his calculations on the experiments of the French physicist, Amagat, who has investigated in great detail the physical qualities of carbonic acid, especially in the neighbourhood of the critical point, Dr Mollier has drawn a complete entropy temperature chart for this substance, including the region above the critical point, and giving lines for the superheating of the vapour. Dr Mollier's chart is reproduced in Fig. 28. The lines with numbers marked upon them are curves of superheating, each at a constant pressure, which the number states in kilogrammes per square centimetre.

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[1] R. Mollier, "Ueber die kalorischen Eigenschaften der Kohlensäure ausserhalb des Sättigungsgebietes." *Zeitschrift für die gesammte Kälte-Industrie*, vol. iii. 1896.

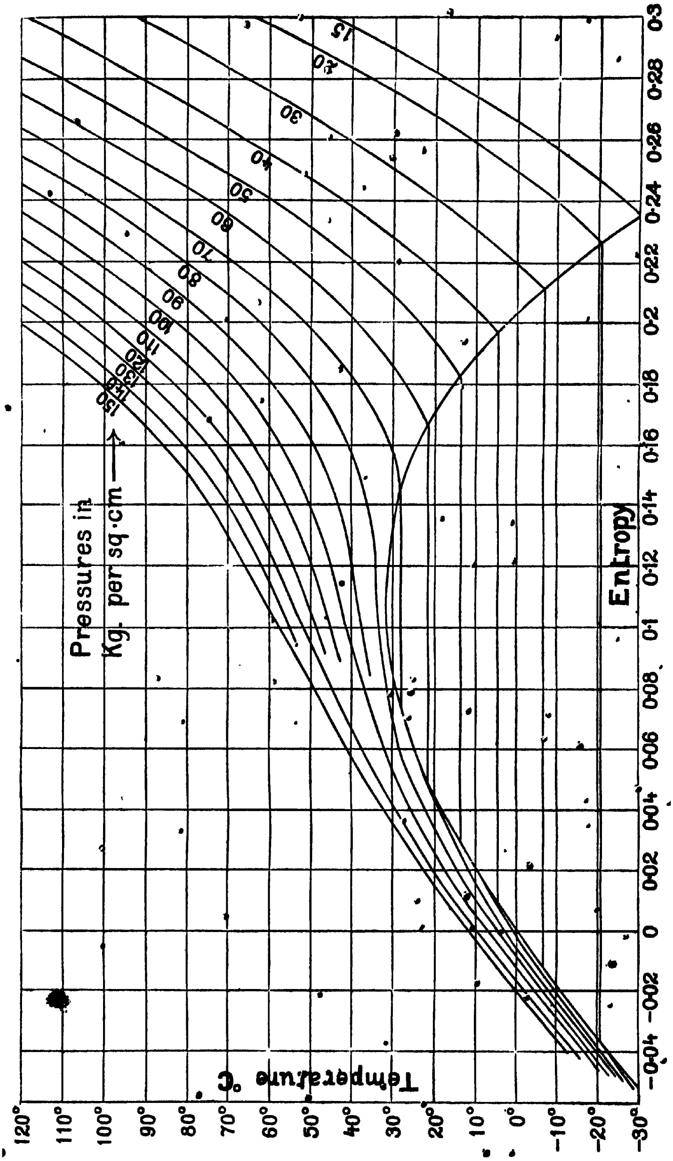

Fig. 28. Entropy-temperature Chart for Carbonic Acid (Mollier).

With the help of this chart it is easy to trace the entropy diagram corresponding to any assumed cycle, involving temperatures which lie above or below the critical point, and also involving any assumed amount of superheating. Inspection of the chart serves to show that when the condensing temperature is near 30° C., not only is dry compression advantageous, but if we were to attempt to prevent superheating, the net refrigerating effect would be *nil.* I cannot pass from the subject without a word of praise for these investigations by which Dr Mollier has cleared up some difficult points in the theory of refrigeration.

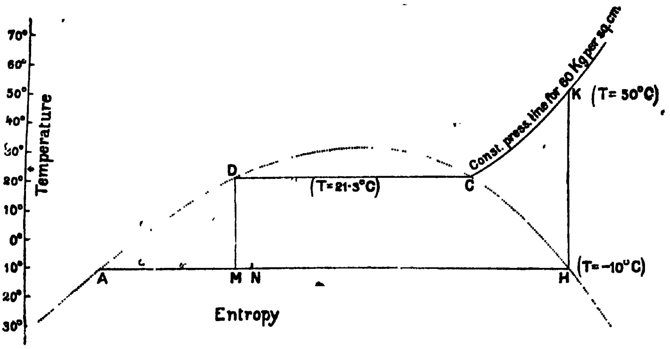

Fig. 29.

As an example of the use of this diagram, take a case where evaporation in the refrigerator goes on at – 10° C., and condensation at 21·3° C., which corresponds to a pressure of 60 kilogrammes per square centimetre (or 853 lbs. per square inch). Assume that the carbonic acid is completely vaporised before compression begins and that the compression is adiabatic. The horizontal line ending at *H* (Fig. 29) represents the evaporating process, and the point *H* represents the state of the substance when compression begins. *HK* is the compression, namely a vertical (adiabatic) line drawn through *H* to meet the constant-pressure curve *CK* for 60 kilos. per sq. cm. At *K*, which is the end of compression, the temperature is found from the diagram to be 50° C. *KC* is the process of cooling the compressed gas, under constant pressure in the condenser. At *C* condensation begins. The process of condensation, which is represented by the line *CD*, is complete at *D*. We shall suppose that no further cooling of the condensed substance takes place, on the high pressure side of the machine. If there were an expansion cylinder, the action in it would be represented by the line *DM*, and in that case the ratio $\frac{MH}{AH}$ would be the wetness after expansion, and the area under *MH* would be the refrigerating effect. But in the absence of an expansion cylinder the net effect is reduced by the heat which the liquid carries over into the refrigerator as it streams through the regulating valve, including the heat equivalent of the work spent upon it as it streams through, consequent on the difference of pressure. The net effect may then be estimated as the area under *NH*, where *N* is taken at such a distance from *M* that the area under *MN* (measured of course to the base-line representing the absolute zero of temperature) is equal to the area *DAM* plus the heat equivalent of the work spent, namely $(p_1 - p_2)$, into the volume of the liquid. [*DN* is a line of constant total heat, see Appendix F.]

[In Appendix F, another diagram is described which was introduced by Dr Mollier in 1904. It affords a still more convenient means of making a quantitative examination of the theoretical action in a refrigerating machine, especially in cases where carbonic acid is the working substance. In that diagram the effect of using a regulating valve instead of an expansion cylinder is readily determined. An example is given in the Appendix.]

It will be obvious from the diagram that there is a material advantage in cooling the condensed substance as far as may be practicable on the high pressure side of the machine, before allowing it to stream through the regulating valve. If such cooling were carried out, it would be represented by continuing the constant-pressure line through *D* downwards: the form of the line would be a curve lying somewhat to the left of *DA*, as is shown in the large scale diagram in Fig. 28. The further down this curve we can go before allowing the gas to expand, the less heat will be carried over through the valve, and the greater will be the net refrigerating effect. This point is one to which particular attention should be paid in practice. Condensation is in general effected at a temperature considerably above the temperature of the cooling water. But it is well worth while, especially when carbonic acid is used, to take pains to get out of the condensed liquid all the heat that can be got out of it before it passes the valve, by passing it through a cooler which is kept as cold as possible by using the condensing water in its coldest available state.

Historical development of the vapour compression process.—Perkins's Machine of 1834.

Leaving questions of theory, we have now to speak of the historical development of the vapour compression process, and of the modern forms taken by vapour compressing machines. The process dates from 1834, when Jacob Perkins patented an apparatus, which is in all essential respects the same as the compression apparatus used at the present time. Sir Frederick Bramwell, in the *Journal* of the Society of Arts for December 1882, has told the story of Mr Perkins's experiments, in which he took part as an apprentice at the works where the machine was built. He has told how with immense effort they succeeded on one occasion in producing a small piece of ice, which he immediately wrapped in a blanket and carried off in a cab to show to Perkins.

Fig. 30 is a sketch based on Sir Frederick Bramwell's description of the Jacob Perkins apparatus of 1834. *P* is the compressing pump which is fitted with self-acting valves. The vapour is compressed into a coil of pipe forming a tubular condenser, *W*, which is surrounded by circulating water. From the condenser it passes, in a liquid state, through the loaded throttle valve, *D*, into a chamber formed by the space between

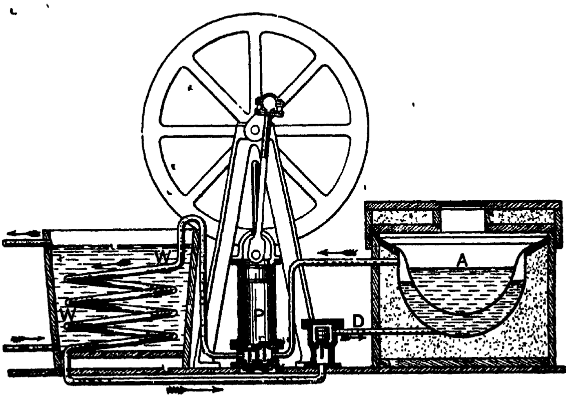

Fig. 30. Vapour Compression Refrigerating Machine by Jacob Perkins, 1834.

the two bottoms of the freezing basin, *A*, where it is vaporised, and from which it returns to the compressor. We have here all the elements of the modern compression machine, and Perkins was no doubt warranted in making the wide claim which is stated in his patent. He claimed (Patent No. 6662 of 1834) "The apparatus or means, as above described, whereby I am able to use volatile fluid for the purpose of producing the cooling or freezing of fluids, and yet at the same time constantly condensing such fluids, and bringing them again and again into operation without waste." The fluid he meant to use was sulphuric ether, but the experiments were made with a liquid produced by the destructive distillation of indiarubber, about which I can learn nothing definite beyond what Sir Frederick Bramwell has told me, namely, that it smelt abominably. It was the intention of Perkins to establish an ice factory in the River Thames by putting some of these machines in barges and driving them by paddles which were to be turned by the ebb and flow of the tide.

Though it must be admitted that this means of getting a supply of power was somewhat visionary, the refrigerating machine in itself was a thoroughly practical invention. As an inventor, however, Jacob Perkins was in advance of his time, and for many years his ideas bore no fruit. It was not until 1857 that the compression process came into commercial application. Then a machine using sulphuric ether was introduced by James Harrison, of Geelong. It is interesting to find a colonial engineer taking this important step in the development of the process, and it is appropriate, for certainly no parts of the world have profited more from mechanical refrigeration than have the Australian colonies. On its introduction by Harrison the ether machine quickly came into considerable use, its manufacture being taken up in England by Messrs Siebe and Gorman. But the ether machine is now obsolete. It had the drawbacks to which reference has already been made. The bulk was large in comparison with machines using other vapours, which came later into vogue. The pressure, both on the high and on the low pressure side, was considerably lower than the pressure of the atmosphere, consequently there was a tendency for air to leak inwards. Finally, the vapour of ether was highly inflammable. It was to take the place of an ether machine at the Bathgate Works that Kirk invented his regenerative air machine, which I described in a former lecture, for the ether machine had produced a catastrophe by allowing the vapour to leak out, filling the room with inflammable gas and causing a conflagration.

Chloride of methyl was proposed as a working substance for a compression refrigerating machine by Vincent in 1878, and was brought into use to a small extent about 1884.

Sulphurous Acid Machine (Pictet).

The sulphurous acid machine dates from 1875, when it was introduced by M. Raoul Pictet. An example of it is shown in section in Fig. 34.

This machine is well known in France and Switzerland, but is not much used elsewhere. Owing to the comparatively low vapour tension of sulphurous acid the construction differs in many points of detail from that of machines using ammonia or carbonic acid. The condenser, *A*, which is much like an ordinary marine condenser, consists of a group of parallel tubes set between two tube plates. The compressed vapour is delivered through the pipe, *D*, to the space surrounding the tubes, while the cooling water, entering at *L*, circulates up through the tubes and down the annular space outside to the exit at *M*. The sulphurous acid passes in a liquefied form through the regulating valve, *K*, to the refrigerator, *C*, which is built up of horizontal drums connected by vertical tubes, and is immersed in a tank of brine. In this example the brine is used to freeze water in cans, one of which is seen in section at *H*. The brine is kept in circulation by the screw pump *G*. The cylinder is furnished with a water jacket to keep down the temperature of the gas during compression. This makes a variation from the simple process of compression and we frequently find the same feature in machines using other vapours. The gas is kept by the jacket from getting so hot as it would do if the compression were strictly adiabatic. Referring back to the entropy diagram, the effect of the water jacket is to bend the compression line backwards. Instead of being straight and vertical, as the line is for an adiabatic action, it is bent to the left as it rises, heat being taken away by the jacket during the compression. Hence the compression line intersects the constant-pressure curve for superheating at a lower point than an adiabatic line would intersect it; in other words, the amount of superheating is less. The work done in compressing the substance is also less. A water jacket is often used in vapour compression machines, whether the working substance is sulphurous acid or another substance. In Pictet's machine, however, the water jacket extends

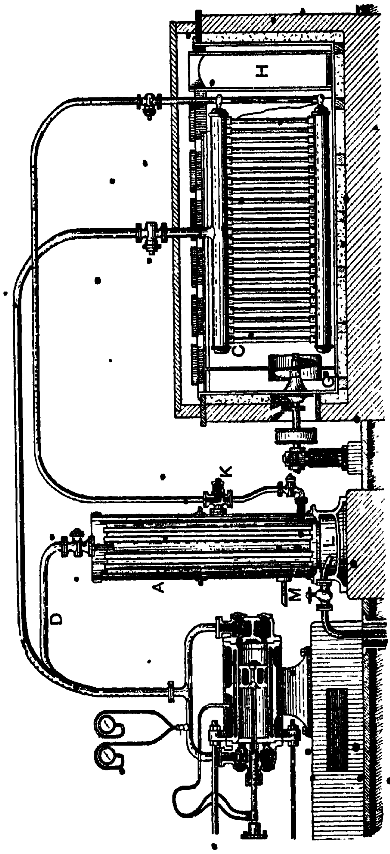

Fig. 31. Pictet's Sulphurous Acid Machine.

not only round the barrel of the cylinder, but also through the interior of the piston and the piston-rod. The piston-rod is hollow, and communicates with the water jacket by means of two flexible pipes. A feature of these machines is the absence of lubrication, it being claimed that the working substance itself acts sufficiently as a lubricant of the cylinder and piston. In his refrigerating practice Pictet has used for working substance a special fluid, consisting mainly of sulphurous acid, but with the addition of about 3 per cent. by volume of carbonic acid.

Ammonia Machines (Linde).

The ammonia machine was introduced by Dr Carl Linde, then a professor at Munich, in the year 1876, and was brought into use in the following year. His English Patent was No. 1458 of 1876. The convenient range of pressure of ammonia and the comparatively small bulk of the machine commend it to general acceptance, and, further, it has, as I have pointed out, a thermodynamic advantage, in giving a cycle which makes a closer approach to the ideal cycle of Carnot than is got with any of the other substances that are practically used. The design of the Linde machine has been carried out with conspicuous care, and it owes much of its great success to excellence in mechanical detail.

A very large proportion of the whole work of refrigeration done for commercial purpose is now done by ammonia compression machines, especially in cases where economy of power is a leading consideration in determining the choice of apparatus. For there can be no question that, whatever the merits of other types, the ammonia compression machine stands easily first as regards the ratio of refrigerating effect to power expended in producing it.

Fig. 32 shows in section a compressor of the characteristic Linde type. It is double-acting, with spring inlet and delivery valves at each end. The valves in the ends of the cylinder are so arranged as to make the clearance space particularly small—something like half of one per cent. of the volume swept through by the piston. This secures a nearly complete delivery of the contents of the cylinder at each stroke. An interesting detail about these machines is the construction of the stuffing-box. To prevent escape of the ammonia the device is adopted which used to be called in steam-engines a lantern brass. The packing is divided into two parts, with a hollow space in the middle, and the space is in this example connected by a pipe with the suction side of the machine. Hence any ammonia which leaks through the inner part of the packing is carried away to the suction side, and not lost, and the outer part of the packing is exposed to no more

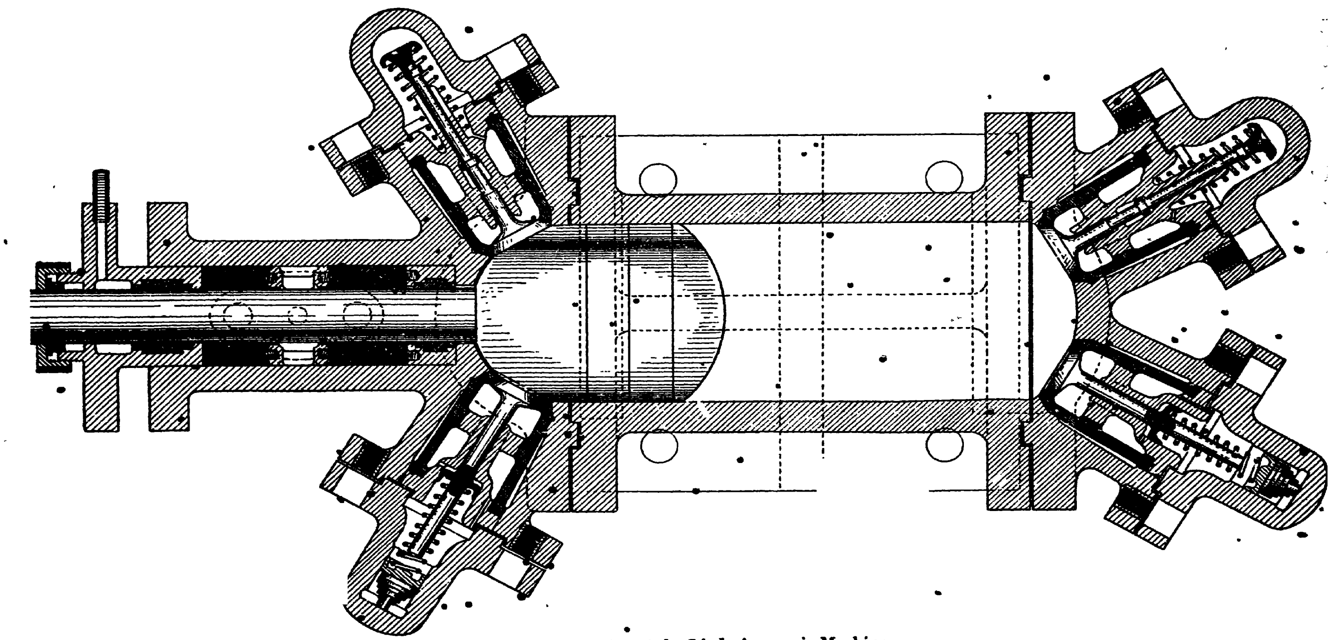

Fig. 32. Compressing Cylinder of the Linde Ammonia Machine.

pressure than the difference between the pressure on the suction side and that of the atmosphere. Any leakage to the outside depends upon that difference of pressure, and not on the much larger difference of pressure which exists between the compression side of the machine and the atmosphere. Another point of importance is the lubrication. Oil circulates through a hollow in the gland, and spreads itself over the surface of the piston-rod. No more oil is used than is required for the lubrication of the piston-rod. In this respect the Linde machine differs from some other examples of ammonia machines, in which oil is injected into the cylinder and is allowed to mix in considerable quantity with the working vapour. [In the later practice of the Linde Company the use of a circulating pump for the oil is abandoned, it being found sufficient to use a sight-drop lubricator which allows a small quantity of oil to enter the cavity of the gland and so lubricate the rod.]

Even here, however, there will be some slight admixture of oil with the ammonia, and as it is desirable to remove the oil before the ammonia is condensed, in order to prevent a deposit which would interfere with the activity of the condensing surfaces, an oil separator is used in the larger sizes of the Linde machine. This is an upright vessel, through which the ammonia from the compressor passes, depositing in the bottom any oil that it brings over. The oil is drained into a second vessel below, which is exposed to the suction pressure only, so that most of the ammonia contained in the oil evaporates before the oil is drawn off. The machine and all parts of the system are made of iron and steel, no brass or copper being permissible. There is no water jacket, for wet compression is used, and the ammonia when it leaves the cylinder is cool. Linde usually makes his compression cylinder horizontal, except in the smallest sizes; the steam cylinder is also horizontal, and drives on a crank set at right angles to the crank of the compressor. This form is preferred to the tandem arrangement of steam and compression cylinders, on the ground that it gives a more uniform crank-effort. With the tandem arrangement the steam-pressure is least when the compressor pressure is greatest.

[In the more recent practice of the German Linde Company the tendency is to use dry compression, and water jacketing is resorted to in the larger machines, but the British Linde Company continues to prefer wet compression, which is claimed to have the advantage that it enables the regulation to be more easily effected which is required to maintain a maximum of efficiency in working, and that it keeps all parts of the compressor cool and so permits of good lubrication.]

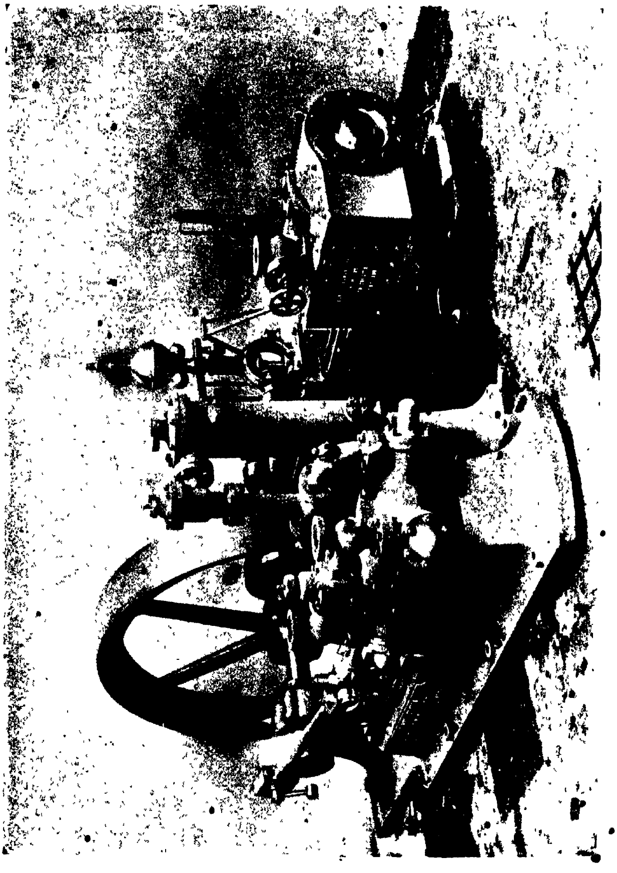

Fig. 33. Linde Ammonia Machine. Marine Type.

In the largest sizes the machines have an ice-making capacity of about 60 tons of ice a day, for a single compressor, but two compressors are not unfrequently combined in one machine. As made for marine use, the compressor is occasionally compound, the process of compression being conducted in two successive stages.

In another form of large machine, a compound horizontal steam-engine is used along with two parallel compressors, each steam cylinder being set tandem with one compressor cylinder. An example of the Linde machine, in one of its marine types, is shown in Fig. 33. In the hands of Dr Linde's companies in England, on the Continent of Europe, and in America, the ammonia compression machine has achieved a very conspicuous success. The result of tests will be quoted, in the next lecture, illustrating the performance of the ammonia compression machine. For use in cases where large amounts of refrigeration have to be effected, its high efficiency gives it preeminence over other types. For use in confined spaces on shipboard, however, ammonia is by no means an ideal working substance, and the question of efficiency gives place to other considerations which often lead to the selection of types in which the co-efficient of performance is less.

Other Ammonia Machines; De la Vergne system.

Other ammonia machines, more or less closely resembling these, are made by the Pulsometer Company, and by Messrs Haslam. In America there are a host of manufacturers of such machines. Some follow Linde without much variation; others adopt a drier method of compression, as for instance the De la Vergne Company, whose machine has a great vogue in the United States, and has also met with considerable success in England, in the hands of Messrs Sterne. This presents a number of interesting points of difference from other ammonia machines, the most characteristic one being the amount of oil injected into the cylinder. The cylinder is vertical, and the clearance spaces, which are comparatively large, are filled with oil. The piston works down into a bath of oil at the bottom of the cylinder. The oil passes through a valve in the piston on to the top, and when the piston rises it carries the oil up with it, forcing it against a movable head at the top of the cylinder, which rises to let the oil escape. Fig. 34 is a section through a De la Vergne compressor. In this case the compressor is single-acting, the lower end of the cylinder being permanently in connection with the suction side of the machine, but double-acting compressors are also used. It is claimed that the oil in this system serves four functions; it lubricates, it seals the glands, the valves, and the piston rings, it gets rid of the effects of clearance, and to some extent it cools the ammonia during compression, much as a water jacket would do, preventing the temperature from rising so high as it would rise if the compression were adiabatic. The ammonia is, however, considerably superheated.

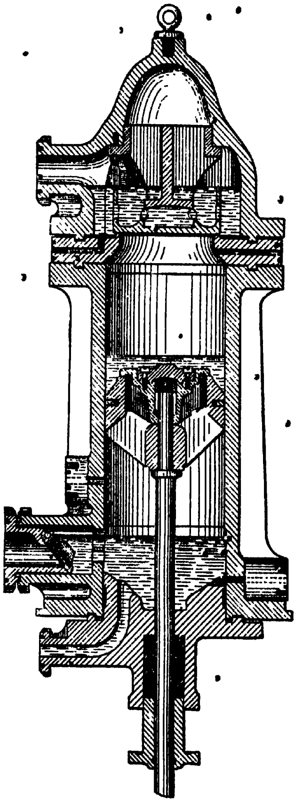

Fig. 34. Single-Acting De la Vergne Compressor.

The avoidance of clearance is scarcely perfect, for oil left in the clearance space, being more or less absorbent of ammonia, gives off a certain amount of ammonia gas during the return stroke, when the pressure is reduced.

The De la Vergne compressor is carried on a frame vertically above the crank, and the steam cylinder is horizontal. The diagram, Fig. 35, is a general view of a De la Vergne apparatus, including an oil-cooler as well as a condenser. The condenser in this example is of a type which practically all the makers of refrigerating machines often use. Instead of being composed of coils submerged in a tank, it is in the form of a group of pipes, arranged more or less horizontally in an open stack, and a fine stream of water is caused to drip over them, while the whole is exposed to the free access of air. This is the "evaporative" or "atmospheric" type of condenser; it is frequently used for stationary plants in preference to the submerged condenser, because it requires very much less water. Such condensers are preferably set on the roofs of buildings or in other places where there is much movement of air: in some cases a fan is used to increase the atmospheric circulation. In condensers of the evaporative type the condensing water absorbs heat not simply by rising in temperature, as it does in a submerged condenser, but by evaporating, and the latent heat of water is so large that the amount of water required is a mere fraction of the quantity that would have to circulate through a condenser of the submerged type. The condenser in this example is divided into a number of sections, from which the ammonia drains into a storage tank, whence it passes through a regulating valve to the refrigerator. It should be understood that the evaporative type of condenser, though it happens to be illustrated here in connection with a De la Vergne plant, is by no means peculiar to that system. The Linde Company rarely use any other type of condenser, and it is a favourite with other makers also, especially when economy of condensing water is aimed at.

The refrigerator in Fig. 35 is made up of a series of pipes, placed in the room which is to be kept cold. The ammonia expands in these pipes, taking heat directly from the surrounding atmosphere of the room. This direct expansion, as it is called, is a usual feature in the De la Vergne plant but is not at all peculiar to it. To aid the expansion pipes in taking in heat from the air their surface is increased in this example by a number of cast-iron discs, but the advantage of these is probably slight after the pipes become coated, as they quickly do, with frozen moisture from the air. [The difficulty with the snow is in fact such that the use of these discs is now generally given up in new plants, and in some cases where they were fitted in the first instance they have been removed.] The oil, which is a characteristic feature in the De la Vergne machine, passes from the compressor to a separating tank, and to a cooler, which is arranged in much the same way as the condenser, in the form of a stack of pipes with dripping water. After being cooled the oil is again injected into the cylinder. There is thus a continuous circulation of oil as well as of ammonia.

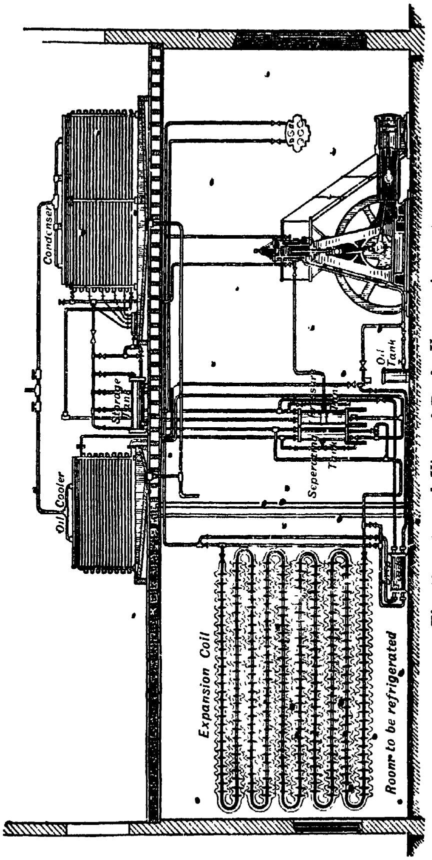

Fig. 35. Ge

There is no question that these machines work exceedingly well, but I am not prepared to say that the excellence of their working is due to the oil circulation. It is difficult, on any ground of thermo-dynamic or other theory, to suggest a reason for expecting any marked advantage to result from this oil circulation, and there is no doubt, on the other hand, that it leads to a material increase in the complexity and cost of the apparatus. [It may be added that in the later practice of this firm the use of oil injection is to a great extent given up.]

Carbonic Acid Machines.

One type of vapour compression refrigerator remains to be spoken of, the highly important type which uses carbonic acid as working substance. Carbonic acid machines were patented by Raydt in 1881, and by Windhausen in 1886. It is proper to mention that Professor Linde was one of the first, if not the very first, to introduce carbonic acid practically as a medium of refrigeration. In 1882 he supplied to Krupp's firm, at Essen, a carbonic acid machine, but he preferred ammonia on thermodynamic and other grounds. The carbonic acid machine is particularly associated with the name of Windhausen. His patents were taken up in England by Messrs J. and E. Hall of Dartford, who have successfully faced the difficult mechanical problems involved in compressing, condensing and re-evaporating, without serious loss, a substance which reaches a pressure of over 1000 lbs. on the square inch in the high-pressure side of the apparatus. Thanks in great measure to good constructive features introduced by Mr F. Hesketh and the late Mr A. Marcet of that firm, the carbonic acid machine has become in Messrs Hall's hands a thoroughly practical means of refrigeration. It is specially suitable for use on board ship on account both of its compactness and of the comparative harmlessness of carbonic acid should leakage take place. The high pressures make it necessary to adopt arrangements which are considerably different from those adopted in ammonia machines. Figs. 36 and 36 *a* give sectional views of the cylinder of a small double-acting carbonic acid compressor by Messrs Hall. Fig. 36 is a longitudinal section showing the piston, the gland, and the two delivery valves. Fig. 36 *a*, which is reproduced here on a somewhat larger scale, is a transverse section showing the suction valve as well as the delivery valve at one end of the cylinder. The construction of the valves will be apparent from Fig. 36 *a*, where the delivery valve is drawn in

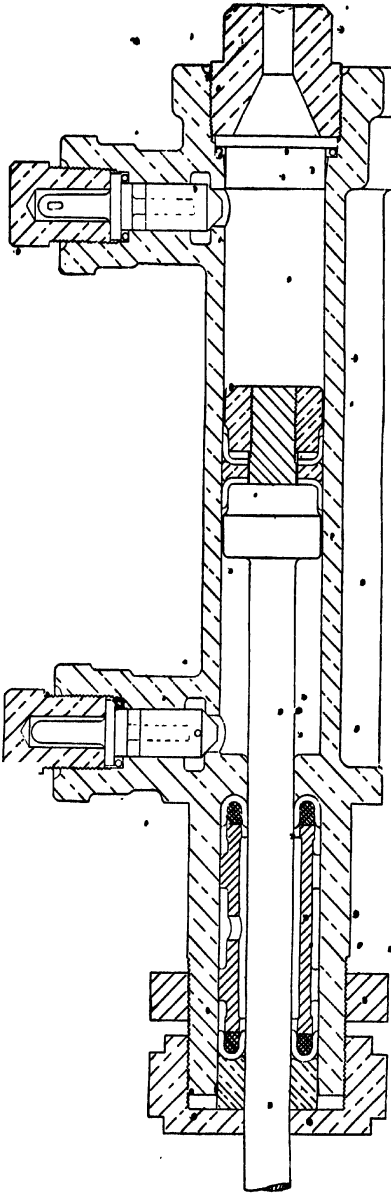

Fig. 36. Longitudinal Section through Hall's Carbonic Acid Compressor.

section. The piston-rod is packed by two cup leathers, a form of packing specially suitable to keep the gas from escaping at the high pressures under which compression is carried on, and similarly the stuffing-box is also packed with a pair of cup leathers, and the space between them—the lantern of the stuffing-box—has oil or glycerine[1] compressed into it which serves as the lubricant. The lubricant is continuously forced into the lantern at a pressure

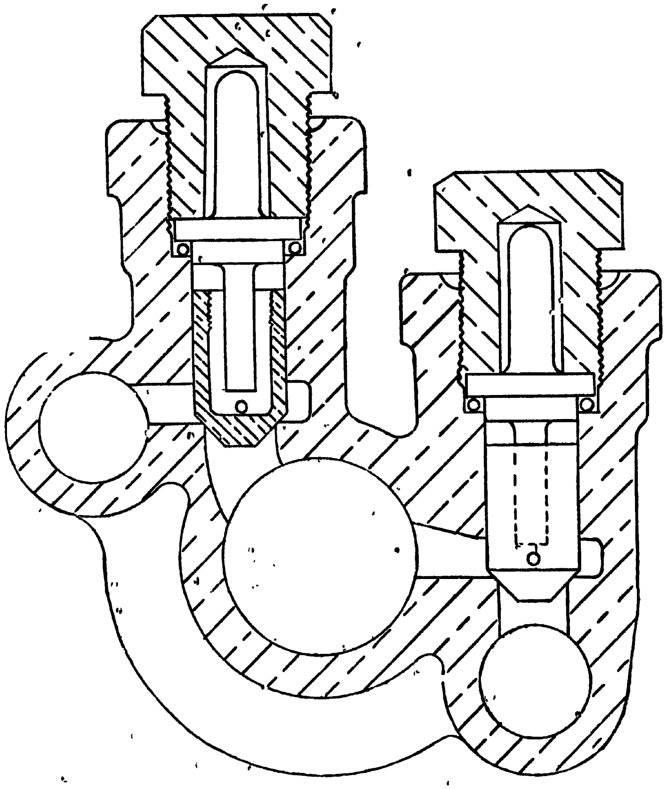

Fig. 36 a. Transverse Section through Hall's Carbonic Acid Compressor.

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[1] The lubricant used at the date of these lectures was glycerine, but Messrs Hall inform me that for some years past they have substituted for glycerine a special oil with a low freezing point (about − 20° Fahr.) as this is more effective and cheaper (1908).

higher than the highest pressure reached by the carbonic acid. Consequently it is continuously leaking in small quantities into the cylinder through the inner cup leather. A small quantity of the lubricant also leaks out through the outer cup leather; but this device secures that the leakage shall be a leakage of the lubricating fluid, and not (mainly at least) a leakage of carbonic acid. The oil is forced into the lantern by means of a lubricator in the form of a differential piston, on the smaller side of which is the lubricating fluid while the larger side is exposed to the full pressure of the gas.

[Metallic packing is now (1908) sometimes employed in carbonic acid machines, and the results as regards reduction of leakage are good. It is claimed that the loss of the working substance is so small that a machine may be kept in constant use for a year without requiring to be recharged with gas,

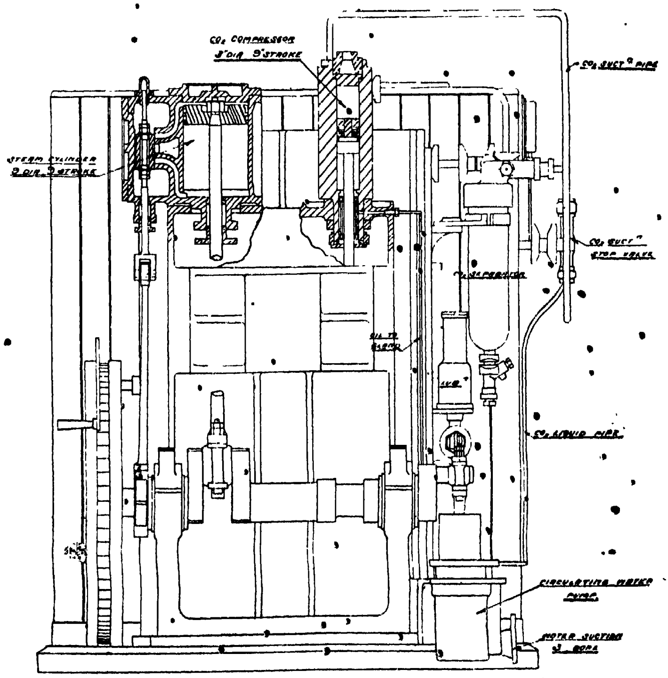

Fig. 87. Hall's Carbonic Acid Machine. Front Elevation.

but though excellent results have been obtained in some instances it appears that most users still prefer cup leathers.]

The small volume of the compressing cylinder and of the working substance makes these machines exceptionally compact. A small carbonic acid machine by Messrs Hall for marine use is shown in section in Figs. 37, 37 *a* and 37 *b*. The steam-cylinder and the compressor are arranged vertically side by side on a casting

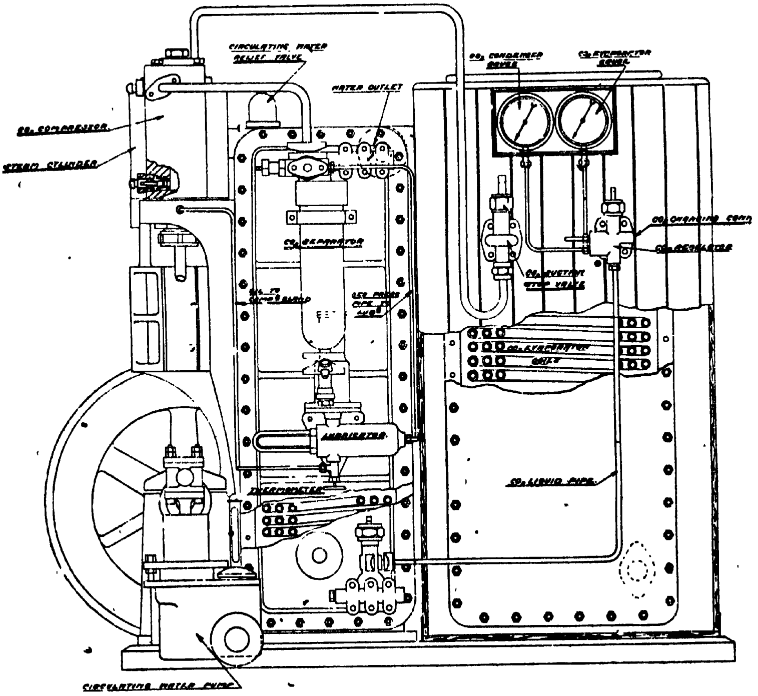

Fig. 37 *a*. Side Elevation.

containing the condenser coils. These are of copper, and behind is another tank containing the evaporator coils, over which a circulation of brine is maintained. At the side is a separator which serves to extract the lubricating oil from the compressed gas.

In small carbonic acid machines the compressor is made out of a gun-metal casting, but in larger forms it is bored out of a solid ingot of steel, cast-iron being unsuitable for this purpose, partly because of the difficulty of getting castings quite free from porosity and partly because it is less easy to get with them the perfect surface of bore necessary for a long life on the part of the piston leathers. A single steel ingot is cut in two to form two compressor cylinders, and thus the porous central portion of the ingot is avoided.

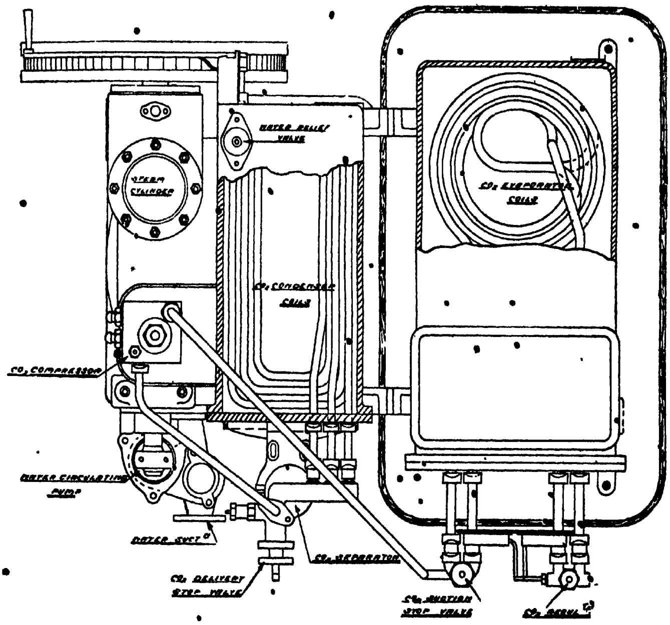

Fig. 37 *b*. Plan.

In the larger machines a pair of compressors are set horizontally, one in tandem with each of the cylinders of a horizontal compound steam-engine. In some the engine is triple, the high and intermediate cylinders being on one rod and the low on the other.

[The manufacture of carbonic acid machines, as an alternative type specially suitable for marine use, has now been taken up by the Linde Company, Messrs Haslam, the Pulsometer Company and other engineers who also supply ammonia machines.]

Absence of an Expansion Cylinder in all practical types of Vapour Compression Machines.

In none of these machines is there an expansion cylinder. The thermodynamic gain which would be secured by its use would, as we saw, not be very great. The theoretical advantage [as may be seen from the example worked out in Appendix F] is not inconsiderable in the case of carbonic acid, especially when the temperature of the cooling water is high. But much of this advantage would be lost in practice through friction in the expansion cylinder, which would not only detract from the work recovered, but would also communicate heat to the working substance and so reduce the gain in refrigerating effect. Another point which affects the question is this, that an expansion cylinder of the proper size for one pair of temperatures would not be suitable for other temperatures. The ratio of volumes swept through by the compressor piston on the one hand, and by the expansion piston on the other hand, would have to depend upon the particular temperatures of the refrigerator and the condenser. It would not be the same when these temperatures varied, and, consequently, in order to get the full advantage derivable from the use of an expansion cylinder in a machine liable to work under various conditions of temperature, it would be necessary to have some means of altering the relative speed of the expansion and the compressor pistons, and that, of course, would introduce very considerable additional mechanical complexity. Mr Windhausen tells me that he has often urged on manufacturers to add an expansion cylinder, but it is scarcely surprising that it is not done.

Mixed Compression and Absorption Machine.

In addition to the various types of machines which we have reviewed, there is a curious compromise type of machine, midway, as it were, between the absorption type and the compression type. This is a machine which has been developed by Osenbrück. He employs what is essentially an absorption machine, but with the addition of a compressor cylinder, which inhales the vapour of the ammonia from the refrigerator, and compresses it to a considerably higher pressure before it is absorbed. In other words, instead of having the pressure in the absorber equal to the pressure in the refrigerator, which is the usual arrangement in an absorption machine, Osenbrück produces a step-up in pressure between the refrigerator and the absorber, the step-up being effected by the agency of a compressor cylinder. I have not heard whether this principle has found application; it seems not unlikely to share the fate which generally attends compromises.

ES. 1922. BENGAL.

LECTURE V.

Trials of Refrigerating Machines.

We have endeavoured to compare the various types of machine from the standpoint of thermodynamic theory, but the conditions in real work are too complex to allow any theory to agree more than approximately with the facts. For more exact knowledge of co-efficients of performance an appeal has to be made to experiment. Trials of refrigerating machines have been carried out, not in great numbers, but in several cases with all possible care, and have yielded data of much value. In the most complete trials three quantities are observed—the work done, the heat absorbed, and the heat rejected. The work done is most directly determined by taking indicator diagrams from the compressor cylinder, just as a steam cylinder is indicated, but with one or two differences in points of detail. For example, in the ammonia machine the indicator should be entirely composed of iron or steel on account of the chemical action of ammonia on brass, and further the connecting pipes which lead to the indicator cylinder itself should be considerably smaller than they usually are in steam-engine work, in order not to add unduly to the volumes of the clearance. The clearance is generally so small in a compressor that unless this precaution is attended to the very act of taking an indicator diagram will alter materially the form of the diagram. There is no serious difficulty in taking good indicator diagrams in ammonia machines, but carbonic acid compressors are more awkward on account both of the smallness of the clearance and the greatness of the pressure. When it is impracticable to indicate the compressor a good idea of the work done in it may be got by indicating the steam-cylinder and allowing for the frictional loss in the engine and compressor. Best of all, however, is a direct measurement (when it can be made) of the power expended in driving the compressor—including not only the work spent in the compressor cylinder, but also the work spent in overcoming friction. Such a measurement is possible when a transmission dynamometer can be introduced between the compressor and the source of power. In electrically driven plant a very close estimate can generally be arrived at by measuring the electrical energy supplied to the motor and allowing for the motor's efficiency in estimating how much of this is usefully transmitted.

The second quantity to be measured in a systematic test is the heat which is given up in the condenser. For this purpose trials are best made with submerged condensers, not with the open-air evaporative condensers which are so largely used in ordinary work. With a submerged condenser, we measure the quantity of cooling water that is used and the amount by which its temperature rises. Suppose, further, that the machine is applied to the cooling of brine or some other liquid. Then, in a precisely similar way we can measure the amount of heat which is taken up in the brine by causing it to circulate through the refrigerator and observing the quantity which circulates in a given time and the extent to which its temperature is lowered in passing through. To make the conditions steady in a trial the brine must in some way be warmed up again before it returns to the refrigerator. The range of this alternate cooling and heating of the brine need not be wide, so that the absorption of heat may take place nearly at one temperature. In the chief experiments which have been carried out specially to test the performance of such machines, the refrigerated brine has generally had its temperature raised by steam-heating—that is to say, it has been removed from the refrigerator into a vessel where it has been subjected to the action of a coil of steam-pipes sufficient to raise its temperature through a few degrees, and then it has been put back into the refrigerator, and so on, a continuous circulation being kept up.

The Thermal Balance-Sheet or Heat Account.

If all these observations are carried out, we have the data for drawing up a thermal balance-sheet for the refrigerating machine. On one side is the amount of heat rejected, Q_1; on the other is the heat absorbed, Q_2, together with the thermal equivalent of the work done, *W*. If we had a perfectly accurate measurement of all the heat rejected, and, again, of all the heat absorbed, and all the work done, the two sides of the account should balance. You never find them balance, and why? Because, in the first place, heat is taken up from the surrounding atmosphere to an extent which we have no means of directly measuring. The brine tank and the pipe leading from the refrigerator to the compressor, and so on, are at a temperature below that of the atmosphere, and however well they are lagged with non-conducting material, we cannot avoid a leakage of heat in from the outside. Then, again, in addition to the work done in the compressor, as measured from the indicator diagram, there is a term which may be of considerable importance, especially in small machines—the work spent in overcoming the friction of the piston rings and gland of the compressor cylinder. This work is given to the working substance as heat, and should form an item on that side of the account on which are summed the heat absorbed by the substance and the work spent upon it.

The discrepancy found in trials between the two sides of the account is of the kind these considerations would lead us to expect. The heat extracted from the brine, plus the heat-equivalent of the indicated work in the compressor, is less than the heat rejected to the condenser, by some 3 or 4 per cent. in the most careful experiments.

Trials by the Munich Commission.

Our experimental knowledge of the performance of refrigerating machines is mainly due to the enterprise of the Polytechnic Society of Munich. More than 10 years ago that Society entrusted a Commission with the task of undertaking trials. The first report of the Commission was issued in 1887[1], the second report in 1890, and there has since been a third briefer and less detailed report issued in 1893. The trials were conducted by Prof. Schröter, who has had an unrivalled experience in such work; they were carried out in the most scientific spirit, and the results command the fullest possible confidence. The report of 1887 deals with a large number of different types of refrigerating machines, which were tested while doing their ordinary commercial duty. Among them were ammonia absorption machines, a vacuum absorption machine using water and sulphuric acid, compression machines of various types, and a Bell-Coleman air-machine. Then in the 1890 report results are given of tests which were made under what one may call more scientific conditions. In the interval between those two reports the Commission established, at the instigation of Prof. Linde, a testing station supplied with every requisite for carrying out trials in the most complete manner. It invited the various makers of refrigerating machines to send their machines for trial, and tests were made on two machines, namely, a Linde machine using ammonia, and a Pictet machine using sulphurous acid. The report of 1893 gives the results of further trials made with another Linde machine embodying all the most recent improvements. In Fig. 38 the chief results of these trials of vapour compression machines are graphically set forth, namely, those in the report of 1890, where a Linde machine and a Pictet machine were tested; and those in the report of 1893, where an improved Linde machine was tested. The curves have been drawn

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[1] *Untersuchungen an Kältemaschinen verschiedener Systeme* (Munich; R. Oldenbourg).

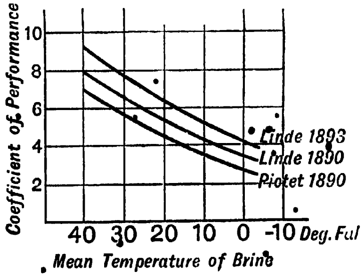

Fig. 38.

to show the co-efficient of performance when the brine had various temperatures. The brine was alternately refrigerated and re-heated by steam, through 3° C., or approximately 5° Fahr., but its mean temperature is taken in drawing the curves. Observe that the ammonia machine was somewhat better than the sulphurous acid machine in the trials of 1890. This is what we should expect from the theoretical considerations already discussed. Further, in the trials of 1893, various small improvements brought about a still higher performance. The results then obtained represent what we may call the high-water mark of refrigeration, so far, at least, as definite tests have been made. It is true that these experiments were made with a comparatively small machine, one taking only about 16 horse-power to drive it, and no doubt better results might be obtained with a larger machine, for in refrigerating machines, as in steam-engines, increased power and size give, within limits, increased efficiency by making the incidental losses due to friction and conduction form a smaller fraction of the whole effect. It is a remarkable fact that the performance is so good in a machine of so moderate a size.

The following Table (p. 107) gives a summary of the results got in Prof. Schröter's final trials of a "12-ton ice-making" Linde machine, driven by a single cylinder steam-engine, which was doing about 16 indicated horse-power. The condensing water was supplied at 10° C. and heated to 20° C. in going through the condenser. The figures relate to four trials, with various brine temperatures, the interval of temperature through which the brine was cooled being 3° C. in each case.

The heat account for one of the trials (the third) is subjoined, the quantities all being stated in British thermal units per lb. of feed supplied to the boiler.

	Thermal Units		Thermal Units
Units of heat rejected to cooling water in condenser	702	Units of heat extracted from brine	565
		Heat equivalent to indicated work in the compressor ...	113
			678
		Balance unaccounted for (being 3·4 % of the whole) ...	24
	702		702

It will be seen that the effective indicated work in the compressor is from 85 to 90 per cent. of that of the steam cylinders—a large proportion. The last two lines in the Table make it possible to compare these performances with those of absorption machines, where heat is directly applied to produce cold. They give the amount of the refrigerating effect on the brine per lb. of steam supplied to the engine, and also the ratio of the refrigerating effect Q_2 to the heat Q supplied in the steam.

Trials of a Linde Ammonia Compression Machine.
(Schröter, 1893.)

No. of Trial	I	II	III	IV
Brine temperature	6° C. to 3° C.	−2° C. to −5° C.	−10° C. to −13° C.	−18° C. to −21° C.
Mean "	4½° C.	−3½° C.	−11½° C.	−19½° C.
" " Fahr. (approx.)	40° F.	26° F.	11° F.	−3° F.
Indicated horse-power (compressor)	14·5	14·5	13·7	12·1
" " (steam cylinder)	16·0	16·7	15·5	14·4
Co-efficient of performance (namely, cold produced, divided by indicated work in compressor)	9·36	7·21	4·98	3·9
Production of cold in British thermal units per lb. of feed supplied to the boiler	1,100	785	565	436
Ratio of heat abstracted to heat supplied $\frac{Q_2}{Q}$	0·97	0·71	0·51	0·39

Comparison of performance of Vapour Compression Machines with other types.

We saw (p. 58) that Professor Denton, in his trials of an ammonia absorption machine, obtained a heat ratio $\frac{Q_2}{Q}$ of only 0·26, and this is the highest figure for such machines of which there is any record. Professor Schröter, in the earlier report of the Munich Commission, made some trials of absorption machines, but obtained somewhat less favourable results. Compare this result with the figures given here for a compression machine. Against the 0·26 of the absorption machine we have about 0·6 as the ratio of $\frac{Q_2}{Q}$ under like conditions as to temperature, for the conditions in the absorption machine trials came about midway between those of the second and third tests in the Table. It may be concluded, so far as we have definite data, that a good compression machine may extract from 2½ to 3 times as much heat as a good absorption machine, both being supplied with equal amounts of heat (in steam), and both working between the same limits of temperature.

Again, if we compare these figures with those relating to air machines of the Bell-Coleman or other types, we find the co-efficient of performance of the ammonia compression machine to be about six times as great as that of the air machine. I pointed out (pp. 36, 41) that Kirk's regenerative air machine had a co-efficient of nearly one, but that the co-efficient in the Bell-Coleman type was more generally 0·6 or 0·7. This is in cold storage uses, when the brine temperature (if brine were used) would be about 15° Fahr. The co-efficient in these Linde trials for this brine temperature is between five and six, or if we take the indicated work in the steam cylinder as the datum of comparison, it is about four or five. That, in round numbers, is about six times as good as anything obtained with an air machine under the actual conditions of cold storage.

Comparison with Ideal Performance.

It is further interesting to compare these figures with the calculated performance of ideal machines. Take as an example the second experiment in the Table on p. 107. The ideal value of the co-efficient of performance of an ammonia refrigerating machine following that cycle, but without any losses other than those which are absolutely intrinsic in the cycle (due to the absence of an expansion cylinder), would be 10·2; the actual co-efficient is 7·2. In other words, the machine as actually tested has an efficiency which is fully 70 per cent. of the ideal efficiency of the process. By the ideal efficiency, I mean the efficiency of the compression cycle working between the same limits of temperature with adiabatic compression and without any incidental losses. It is a very remarkable fact that the real machine should be able to achieve 70 per cent. of the efficiency of an ideal machine. If we turn to the steam-engine, we find in general that the proportion between the real performance and the ideal performance is not so good as this, and if we turn to any other form of refrigerating machine, the absorption type or the air machine, we find that the real performance is a very much smaller fraction of the ideal. One may say that a strong point to the credit of the ordinary compression type of refrigerating machine is that it is able in practice to approximate nearly to its own ideal as well as having an ideal not far short of the perfect Carnot ideal. If we compare the experimentally-found co-efficient of performance with the ideal of the Carnot cycle, we find that with the same limits of temperature the actual performance comes to over 68 per cent. of that perfect standard. There is, therefore, no very great margin for improvement in the performance of such a machine. The real performance must fall short of the ideal for reasons which have already been suggested. There is loss through conduction of heat from outside to cold parts of the machine. There are losses due to the friction in the cylinder, and there is the loss which proceeds from exchanges of heat between the working substance and the metallic surface with which it is brought in contact during compression. This is an action like that which steam engineers fully recognise now-a-days as occurring between the steam in an engine and the cylinder walls. The exchanges of heat there result in a diminished efficiency of performance, and in the same way the general effect of the exchanges in a refrigerating machine is to take something away from the performance as calculated from an adiabatic process.

Further Data from Trials.

In addition to these important results published by the Munich Commission, certain other data are available, which are in general accordance with them. Professor Denton has published in vol. 12 of the "Transactions of the American Society of Engineers" a test of a much larger ammonia compression machine, made by the Consolidated Ice Company, working with a process of dry compression, and, therefore, differing in this detail from the Linde process. He found a co-efficient of performance which comes between the Linde results of 1890 and those of 1893. This bears out the remark made in discussing wet and dry compression to the effect that from the theoretical side it does not much matter whether the process is conducted in the Linde manner with wet ammonia, which remains saturated during compression, or with dry ammonia, which becomes superheated. I said that the dry process was theoretically a little less efficient than the wet, and Professor Denton's tests, although made with a larger machine than either of the machines used in those tests, did in fact give a result somewhat inferior to the best tests obtained with the smaller Linde machine.

Tests of a Small Ammonia Machine.

Through the kindness of Mr Lightfoot, I have been able to make some tests in the Engineering Laboratory at Cambridge with a small ammonia compression machine of the Linde type. No results seem to have been published hitherto for a quite small ammonia compression machine. In this case the machine took only about 1½ horse-power; it is nearly the smallest machine made by the Linde Company. The trials were carried out in a manner very similar to Professor Schröter's, except in one particular where the procedure was novel. The brine, instead of being taken out of the refrigerating tank, heated, and put back again, was continuously heated while it was in the refrigerating tank by electric means. A number of cans in the brine tank, which usually serve for ice-making, were partly filled with frames containing incandescent electric lamps. These cans were immersed in the brine, and were fastened down by the non-conducting cover of the tank. The lamps, when excited by the electric current, heated the brine, and the current was adjusted so that the heating by the electric lamps exactly balanced the cooling by the refrigerating machine. There was no practical difficulty in adjusting the electric current to keep the temperature of the brine steady, and when such a state of balance was arrived at then the amperes and volts of the current showed how much heat was being given to and taken from the brine. The method has the advantage of allowing a trial to be made in a very short space of time. A sensitive electric thermometer, consisting of a coil of wire whose resistance was continuously measured, was spread about through the brine tank, and served to show at once any small variation of temperature. The results show that in a small machine of this kind with a brine temperature of 23° Fahr. the co-efficient of performance was 3·2, whereas with the same brine temperature the co-efficient ranges from 5 to nearly 7 in the larger machines tested at Münich. The difference is to be explained by the fact that this is so much smaller a machine. The compressor horse-power was only about 1½, and friction played a relatively large part. We can no more expect to realise a good approach to the ideal in a small refrigerating machine than we can expect a steam-engine of two or three horse-power to give figures representative of the efficiency of a large engine. For so small a machine it is an excellent performance to obtain, with brine at a temperature of 23°, an amount of cooling which is more than three times the amount of the work expended in driving the machine. The heat account in these trials shows a relatively large unaccounted-for balance, and that again is what theory would lead us to expect.

Trials using Carbonic Acid.

Turning next to tests of the carbonic acid machines, we find a comparative paucity of data. There are not by any means the same number of figures available as to the performance of carbonic acid machines. Mr Windhausen has been kind enough to send me particulars of early experiments made by him mainly to determine whether carbonic acid was capable of acting effectively with comparatively high temperatures of condensing water. The experiments gave satisfactory assurance as to this point. Mr Hesketh, in his paper read before the British Association in 1895, gives the results of a number of tests made by Messrs Riedinger, German manufacturers of the Windhausen type of carbonic acid machine. For the purpose of making a comparison between the heat extracted and the work expended in carbonic acid machines, data are to be found in an important paper by Dr Linde, who has carried out a series of tests making a direct comparison between an ammonia machine and a carbonic acid machine when both were working under as nearly as possible the same conditions[1]. He found when the temperature in the condenser was 72° Fahr., and the temperature of the brine was the same in both cases, viz., about 15° Fahr., that the co-efficient of performance in the carbonic acid machine was 82 per cent. of the co-efficient of performance in the ammonia machine, and that when the temperature in the condenser was raised to 95° Fahr., so as to be above the critical temperature of carbonic acid, then the co-efficient of performance was just 50 per cent. of that of the ammonia machine working between the same limits of temperature. Now, the relative efficiency of the two, as given by these figures, agrees remarkably well with what theory would lead us to expect. Professor Linde further found that if he artificially cooled the condensed liquid before allowing it to pass through the regulating valve until its temperature was lowered to that of the refrigerator itself, then he got substantially the same amount of refrigeration whether he used ammonia or carbonic acid. That, again, is the conclusion to which theory points. The difference in efficiency in the two substances is chiefly due to the different amounts of heat which the two liquids contain when they leave the condenser. If we could prevent either substance from carrying any heat into the refrigerator in passing the regulating valve, there would be no difference between the two in the efficiency of their working. Under the ordinary conditions of working, we do not and cannot prevent this conveyance of heat, and then there is a difference which is comparatively small so long as the condenser temperature is low, but becomes large, reaching something like 50 per cent., under tropical conditions of condenser temperature.

Other Ways of stating Performance.

An alternative mode which might be followed in stating the efficiency of refrigerating machines is to give instead of the co-efficient of performance the number of thermal units of refrigerating effect per horse-power hour. To get this figure in British units it is only necessary to multiply the co-efficient of performance by 2545. Frequently the performance of machines is expressed with reference to ice-making. If you take 1 lb. of ice as requiring about 200 thermal units for its production—that is to say, 142 thermal units for the actual process of freezing, and the extra 58 or so for the preliminary cooling of the water and for the cooling of the ice below the temperature of freezing—you will find that the best results which are stated here correspond to a production of about 15 lbs. of ice per lb. of coal used. From 15 lbs. to 20 lbs. of ice per lb. of coal is the largest return that can be looked for in view of the results of the Munich experiments.

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[1] *Zeitschrift für die gesammte Kälte-Industrie*, 28 Jan. 1895, or *Zeitschrift des Vereins deutscher Ingenieure*, 2 Feb. 1895.

I have been interested to hear from Mr Lightfoot that in the Linde ice-making factory at Hull, they are actually able to obtain 15 tons of ice by the consumption of one ton of coal. This, it should be added, is under conditions that are more favourable to economy of power than hold in most cases. Generally it is required to produce clear, transparent ice, and the water has to be distilled, and also to be stirred during the freezing. This is not necessary at Hull, for the ice made there is in the form of opaque blocks which are used in preserving fish. When it is necessary to make the ice transparent the output per ton of coal will not be so large.

[Mr Lightfoot informs me in 1908 that in an ice factory at Milford, where a Linde plant is employed making 48 tons of ice a day the output in regular work is 18 tons of ice per ton of coal. This is probably the best result that has been obtained with a steam-driven plant.]

Uses of Mechanical Refrigeration.

I pass now to speak briefly of the various uses to which mechanical refrigeration is put. Perhaps the best indication of the extent and variety of these uses may be given by quoting from a statement issued by the Linde Company regarding the use to which 2600 of their machines have been put. Out of those 2600, it appears that 1406 are employed in breweries, 403 are employed in cooling land stores for meat and provisions, 204 are employed in cooling ships' holds for the purpose of transporting meat and provisions, 220 are employed in ice-making, 73 in dairies for butter-making, 64 in chemical factories, 17 in sugar-refining, 15 in candle-making, and 198 for "various purposes." It appears on analysis, that the "various purposes" include chocolate manufacture, glue-cooling, rubber-cooling, skating rinks, manufacture of dynamite and cordite, manufacture of gelatine plates for photography, the keeping cool of the eggs of the silkworm until the mulberry leaves are ripe, and also such special uses as that which is known as the Poetsch process of sinking shafts. This is a peculiar and interesting application of refrigeration which may be noticed in passing. When a shaft such as a coal mine shaft has to be sunk through water-bearing strata, particularly through quicksands, one of the most convenient ways of doing it is to refrigerate the circumference of the shaft, and thus keep out the water by maintaining a hard frozen shell round the portion which is being excavated. A similar process was successfully used in 1885, by Captain Lindmark, of the Swedish Royal Engineers, in the construction of a tunnel at Stockholm.

Uses in Brewing.

The use in brewing has been the sheet anchor of the mechanical refrigerating industry. It has employed probably more than half of all the refrigerating machines that have been built. In British breweries mechanical refrigeration is principally employed for cooling the wort through the medium of what is known as the Baudelot cooler; the wort is made to trickle over a series of pipes through which cold water is being circulated, this water having been previously cooled by means of a refrigerating machine. In exceptional cases the cooling of the wort is directly performed by letting it trickle over a stack of iron pipes in which ammonia is evaporated, instead of using cold water as an intermediate agent. On the continent of Europe, and in America, where lager beer is brewed, and a lower temperature is needed in the various processes of brewing, fermenting, and so on, we find refrigeration applied to a greater number of purposes than is usual in English breweries. It is used not only in the Baudelot coolers for the wort, but also in the so-called "swimmers" in the fermenting vats, and also for keeping the beer cool in the cellars. In small breweries ammonia absorption machines are not uncommon, but where the work is to be done on a large scale the compression machine is preferred, and generally the tendency is for the compression process to oust the absorption process.

Transportation and Storage of Meat.

Next to brewing, the largest use to which refrigerating machines are put is the cooling of air for the purpose of storing and transporting meat and other provisions. The freezing of beef and mutton for cold storage is accomplished by cooling the atmosphere in which the carcases are hung, and continued exposure to a cold atmosphere is all that is necessary to preserve them. When meat is cooled down to a temperature approximately equal to, or below, the temperature at which water freezes, the ordinary processes of decay and decomposition are completely arrested. I understand bacteriologists to say that the septic germs may still be present and alive, but they are quiescent. They are hibernating as it were—not killed. Indeed, according to Prof. Dewar, you may expose germs to the vastly lower temperature of liquid air, and find them still alive when they are thawed. In any case it is certain that a moderate degree of cold serves to prevent or arrest the decomposition in meat, so that it may be kept in a cold atmosphere for any length of time without loss of freshness. Since 1879, when the first small experimental cargo of frozen meat was brought from the Antipodes, the trade has grown to immense proportions.

There is not only an immense quantity of frozen mutton brought from Australia, from New Zealand, and from the River Plate, as well as much frozen beef. There is also a large importation from America of what is called "chilled" beef, which means beef not actually frozen hard, but kept at a temperature low enough to prevent decomposition for a time. Beef or mutton brought through the tropics is frozen hard before shipment, and is kept frozen during the voyage. But this is not found to be necessary when only the Atlantic is to be crossed. It is enough in that case to reduce the carcases to a temperature approximating to 32°, but not so low as to freeze the interior, and beef thus treated is said to be chilled, to distinguish it from the frozen beef which comes from Australasia or from the River Plate. The trade in frozen mutton gives employment to a great fleet of ships of large tonnage, whose holds are kept at a temperature of something like 20° Fahr. during the voyage. In order to prepare beef for a voyage of this sort the carcases are subjected to a temperature for several days of from 10° to 15° Fahr.

The diagram, Fig. 39, shows observations taken by Mr Lightfoot during the freezing of beef by subjecting it to a temperature which is indicated by the lowest of the curves, the temperature of the room in this case being approximately 10° Fahr. The temperature of the beef was at first 55°, it fell during the first 24 hours to 32°, then continued to fall slowly to 30°, and remained for more than 24 hours at that temperature, showing that the freezing was then going on. After that it resumed its fall, as the substance had then become completely frozen. It appears from this curve that the freezing point of beef is something like 30°, and that the freezing proper of a piece about 12 in. thick takes two or three days when the atmosphere in which it hangs is at about 10° Fahr.

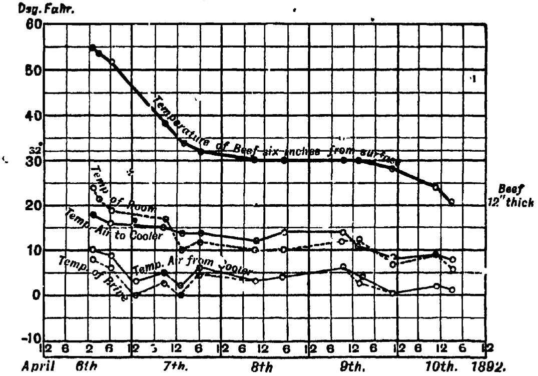

Fig. 39. Process of Freezing Beef.

Cold Stores.

The development of this trade has led to the creation of a large number of cold stores for the reception of the beef when it arrives, in addition to the freezing chambers into which it has to be put before it is shipped. One of the largest of the numerous cold stores in London is that of the Victoria Docks, which is made up of three separate box-shaped buildings of two storeys, covered by a roof with large projections, which cut off the walls effectually from the sun's rays. The rooms themselves are, as in all such stores, insulated by a considerable thickness of non-conducting material.

Each of the three stores has its engine and refrigerating machine in the middle, and the plant is especially interesting as a survival of the application of the air process. The machines are of the Bell-Coleman type, by Messrs Haslam; they take up approximately 200, 200 and 300 horse-power. It is safe to say that this type of refrigerating machine is one not likely to be introduced in the future into any large stores on land, not because it does not do its work thoroughly well, but it takes a needlessly large amount of power to do it[1].

Fig. 40 gives a sectional view of another great cold store, the largest single building of the kind in London. It is the store at Nelson's Wharf designed by Sir Frederick Bramwell and Mr Harris, and refrigerated by a pair of ammonia compression machines of the De la Vergne type. One admirable feature about the design of this store is that it has no openings except at the top. The process of introducing and removing the frozen carcases is performed through openings upon the top floor, where the cranes appear in the sketch. The store proper consists of the five storeys below this floor, three of these storeys being above the neighbouring ground level, and the other two under it. The cold rooms are in all 45 ft. deep, and about 150 ft. by 150 ft. in plan, and give a storage space of some 700,000 sq. ft. They are thoroughly insulated by non-conducting material all round the sides, under the lowest floor, and over the ceiling floor. This arrangement has been adopted in recognition of the fact that the most convenient way of keeping a store cold is to make it a well of still air. The air in its cold state is something like 1-12th heavier than an equal volume of atmospheric air, and, consequently, if there are any openings near the bottom, air would stream out just as a heavy liquid streams out of a hole made in the side of a cistern. In this case the cold air is kept in by the simple expedient of having no openings whatever, except the openings at the top. The frozen carcases are brought alongside in barges, and are raised to the top floor by ingenious mechanical ladders, in the form of endless chains, on the moving rungs of which the sheep are placed. From the top floor they are dropped down into the various chambers. In this store the refrigeration is performed by the direct expansion of ammonia without using brine.

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[1] The cold stores at the Victoria Docks, as well as several other cold stores in London, are described in a paper by Mr H. F. Donaldson, published in the Minutes of Proceedings of the Institution of Civil Engineers, Feb. 9, 1897.

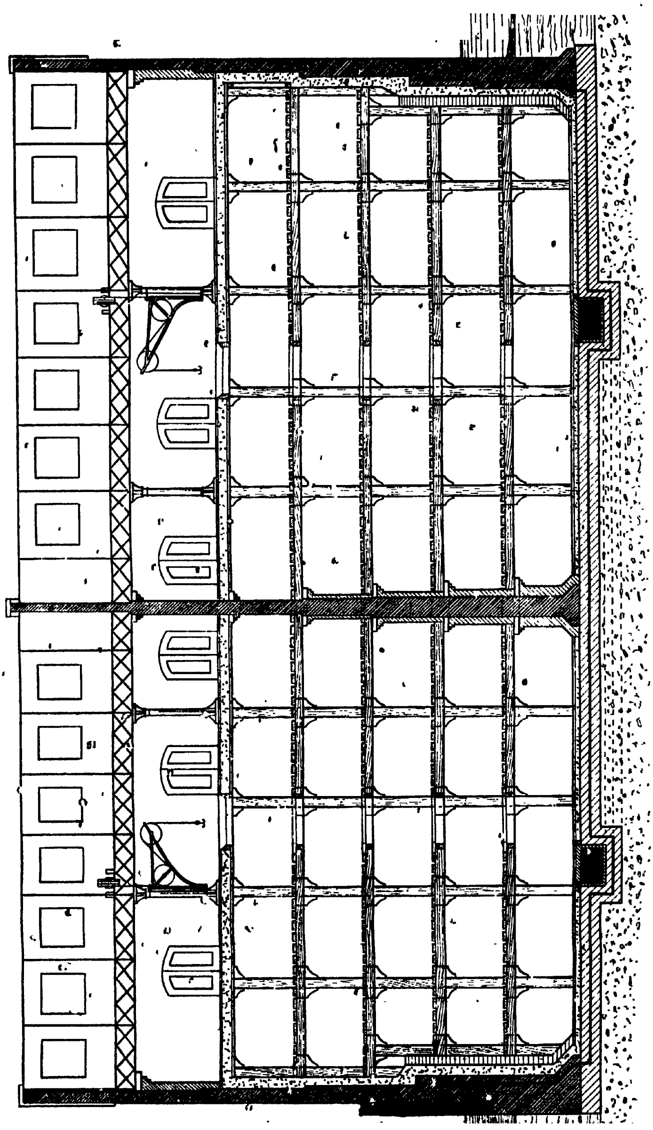

Fig. 40. Cold Store at Nelson's Wharf.

Each storey is cooled by a network of ammonia pipes arranged along the ceiling.

At the time the machinery for this store was arranged, confidence in the system of direct refrigeration by ammonia was not so great as it is now, and a supplementary plant was placed in the engine-room, viz., a large cold air machine of the Bell-Coleman type by Messrs Haslam. The air ducts connected with that machine appear in the drawing at the bottom of the building. I understand that the cold air machine is not now used. It has been found that there is no need to maintain a circulation through these chambers; the still cold air produced by the ammonia pipes answers the purpose well in this particular case. Here nothing is brought in except carcases which have already been frozen hard. The conditions, therefore, are very different from those which hold in a store where provisions are placed in a soft state. Where that is the case there is an advantage in having the air in circulation, especially when provisions are liable occasionally to enter in a state of incipient decay. In such cases, a movement of the air is good, but it is easily accomplished without resorting to an air machine for refrigeration. As to the advantage in point of efficiency of an ammonia machine, the contrast is sufficiently obvious when you consider that in the Victoria Dock Stores, and in these stores of Nelson's, there is practically the same capacity for carcases. The size of the two is almost identical. In the Victoria Dock Stores there are three air machines, requiring an aggregate of about 700 horse-power. In this store, of Nelson's, as I saw it, a single ammonia machine, working at 30 or 35 horse-power, was performing the whole of the refrigeration. It should be added that part of this difference is due to the design of the stores, and part to the economy which comes of using ammonia as the working substance. Now, this economy in power may be retained along with the condition of circulation of air, and in a great number of cold stores this is actually done.

Cooling of air by direct contact with cold brine.

Among plans followed by the Linde Company in the refrigeration of other stores, and also on board ship, the device has been used of causing the ammonia to expand in a coil contained in a brine tank, in which there are revolving drums, the surfaces of which project into the air above. Over these a current of air is maintained by a fan; air, namely, which comes out of the store, and goes back to it again after being cooled by passing over the drums. In other examples, instead of drums, a large number of revolving circular discs are arranged side by side parallel to one another on an axis, dipping into the brine tank, and bringing up their cold wet surfaces for the air to blow over. In the most recent examples, Mr Lightfoot employs a still simpler arrangement. There is a stack of pipes in which the ammonia is being expanded. Over that stack a drip of brine is playing, and between the rows of pipes there are plates, so that the chilled brine which splashes off the pipes wets the surface of the plates. The air is blown through a chamber containing this stack of pipes and plates. It is, therefore, brought into intimate contact, not only with the wet surface of the pipes on which the brine is playing, but also with the wet surface of the plates, and thus the air meets a large surface operating to chill it. All these arrangements have an indirect advantage in this respect, that not only do they bring the air into very intimate contact indeed with the cold material, and lower the temperature nearly to the lowest point reached by the ammonia, but, further, that they clean the air. When the air comes in contact with cold wet surfaces it deposits moisture, because the wet surfaces are cooler than the air itself, and it also tends to deposit any germs or other impurities which may be suspended in it. The brine is found to exert a purifying effect on the air, which goes back to the chamber to a certain extent filtered, deodorised, and disinfected. It may be added that the plan of bringing the air into direct contact with the cold brine does not, as might perhaps be supposed, tend to make the atmosphere of the store damp, for though it is saturated at the very low temperature of the brine the amount of moisture which it then contains is so small that at the higher temperature of the store it is far from saturation.

Heat Insulation of Cold Rooms.

We shall see later that the most effective way to stop the passage of heat into a chamber is to surround it with a space empty of all matter; in that case it is only by radiation that heat can enter at all. But this is impracticable in the case of a cold store. In air, or for the matter of that in any gas, the conduction of heat goes on very slowly, and if we could have an air space in which the air was perfectly still it would form an admirable insulating wall. Convection currents are, however, set up in any wall of air enclosed so as to form the lining of a cold room. Suppose we have such an air space, enclosed between layers of match-boarding; the inner layer separating it from the cold atmosphere of the store while the outer layer separates it from the external wall. That portion of the enclosed air which is in contact with the cold inner woodwork will continually be streaming down, while that portion which is in contact with the warmer outer surface will continually be streaming up, and thus a circulation will be maintained which stirs the air, and in great measure destroys its value as an insulator of heat, by making convection accomplish the transfer which conduction proper would not do. A much improved effect is obtained when the air space is divided up by means of intermediate partitions. And an effective way to keep the air nearly still is to pack the space more or less closely with some finely divided material such as flake charcoal or granulated cork or silicate cotton—the spongy fibrous product formed by making a powerful steam-jet act on a stream of molten slag. Such a material is in itself a worse insulator than air, but its action is like that of a multitude of partitions placed exceedingly close together. The whole space is still largely filled with air, in the pores of the charcoal or of the silicate cotton, but by being entangled in the pores the air cannot circulate in convection currents. The function of the porous packing is to keep the air still. But to act effectively the material must itself be a poor conductor of heat in the solid or closely grained state, else the advantage which it secures by preventing movement of the air will be counterbalanced by the conduction that takes place through its own substance[1]. A point of great practical importance is to keep the air spaces and the insulating packing dry: any moisture tends, no doubt by alternate evaporation and deposit, to impair the efficiency of the insulation. The enclosing partitions are often made in double layers of match-boarding with waterproofed paper between. A common arrangement is to make them enclose a space six inches wide which is filled with silicate cotton, charcoal or other porous insulator. In American practice the porous material is sometimes dispensed with and a series of parallel partitions with narrow air spaces between are used instead.

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[1] For experiments on the thermal insulation secured by various materials see a paper by Lamb and Wilson in the *Proceedings of the Royal Society* for 1899, p. 283.

Cold Storage in Ships.

On board ship the considerations governing the selection of refrigerating plant are, of course, different in several ways from those that apply on land. There the ammonia machine, the carbonic acid machine, and the cold air machine all, to a certain extent, maintain their position as rivals. No one of them can fairly claim to have displaced the others. Each has distinct merits from the point of view of the superintending engineer of a line of steam ships. The advantage of dispensing with the use of what he would probably call chemicals may lead him to prefer the air-machine in cases where economy of coal is a secondary consideration. If he wishes to secure the greatest economy of coal he will prefer ammonia. If he has to place the refrigerating plant in the engine-room, he will be afraid of the possible escape of a substance which would be, at all events, disagreeable and embarrassing if it escaped there, and his choice is more likely to fall on carbonic acid. When the machine can be separately housed in a part of the ship where any escaping fumes would not cause serious inconvenience, ammonia machines are suitable. In the engine-room however an ammonia machine would be out of place; for such a situation as that a carbonic acid machine would be open to far less objection. Even a large volume of carbonic acid gas may be allowed to escape into an engine-room or other such confined space with comparative impunity, whereas a serious leakage of ammonia would make it untenable. [The Board of Trade have now made a rule that when ammonia machines are used on board ship they must be enclosed in a separate compartment. Hence for small plants such as are wanted to keep provisions fresh in passenger steamers carbonic acid machines, which may be placed in the engine-room or in any convenient place, are now almost exclusively used. But in cargo steamers engaged in the frozen or chilled meat trade ammonia machines are often found, the separate compartment in which they are housed being generally on deck. Thus with one or two exceptions the vessels employed to bring chilled or frozen meat from the River Plate are fitted with ammonia machines, and some of the largest meat-carrying companies in the Australian and New Zealand trade also use nothing but ammonia.]

Defrosting.

The quality of frozen beef, from the consumer's point of view, depends a good deal on how it has been thawed. At Nelson's Wharf an ingenious arrangement has been introduced for the purpose of what is technically called "defrosting" the beef. The beef to be thawed is hung in a special chamber, where a circulation of air is maintained over cold pipes, on which a deposit of moisture takes place, and then over warm pipes, by which the temperature of the air is raised before it again comes into contact with the beef. In this way the beef is subjected to an atmosphere which is warm enough to produce the desired thawing, and yet, at the same time, is dry, and is maintained dry, notwithstanding the amount of moisture it takes up from the beef itself. The object is to keep the dew point of the atmosphere lower than the temperature of the surface of the beef, and consequently to prevent moisture from being deposited upon the surface. In the ordinary thawing of beef by simply hanging it in a natural warm atmosphere, a deposit of moisture takes place which deteriorates the quality. This is prevented by regulating the temperature of the air in relation to its dryness. In Nelson's defrosting process it is kept dry by being made to give up its moisture to the cold pipes, before it is warmed by the hot pipes to the temperature proper for thawing.

Fish and Fruit.

Mechanical refrigeration is applied to a limited, but increasing, extent in the importation of frozen fish. Trawlers are in some cases supplied with refrigerating plant, and the fish when they are caught are plunged alive into cold brine, which freezes them solid. More commonly trawlers are supplied with ice for the preservation of their catch. [Trawlers that go far afield for their catch carry refrigerating machines which keep the holds cold by circulation of air, but at a temperature not low enough to freeze the fish.] Refrigerated fruit is imported from Tasmania and Jamaica, not at a temperature sufficient to freeze it, but at 50° or

55° Fahr., which is found to be low enough to prevent decay, without unduly drying the fruit or injuring its flavour. As a *tour de force* flowers have even been brought from the Antipodes, enclosed within blocks of ice, and retaining, apparently, their original bloom.

Ice-Making.

In the application of mechanical refrigeration to ice-making, two general methods are employed, the can system, and the cell system. In both cases brine forms, as a rule, the medium by which heat is carried from the water to be frozen to the refrigerating agent. The broad distinction in the two methods is, that in the can system the water is enclosed in a number of cans or moulds which are immersed in an open brine tank, whereas in the cell system the brine is enclosed within a number of hollow walls, and between these are open spaces filled with the water to be frozen In both cases, in order to produce clear ice, the water has to be agitated during the freezing Under ordinary conditions water contains a considerable quantity of air dissolved in it; and as the temperature is lowered, and the water is frozen, this air is given out. If the water is at rest, and especially if the freezing goes on rapidly, the bubbles of air get caught and frozen into the mass, with the result that the ice is opaque. This may be partly prevented by having the water distilled in the first instance to get rid of all foreign matter, including air; and even if the water is not distilled the opacity can, to a great extent, be avoided by keeping the water in movement while it freezes. To get the clearest possible ice, both precautions are sometimes taken; the water is both distilled and agitated.

One of the most approved methods of keeping the water in ice cans moving is illustrated in Fig. 41. The action here is pneumatic; the reciprocating motion of the air-pump piston causes a portion of the water in each can to be alternately sucked up into a small reservoir on the branch pipe dipping into the can, and returned to the can. In other cases mechanical stirrers are used which are lifted out when the freezing of the block approaches completion. The ice-crystals grow from the sides of the mould inwards, and the direction of their growth is marked by the form taken by the imprisoned air-bubbles, which are found to some extent even in comparatively clear ice. The bubbles are drawn out into long, fine tubes, pointing inwards from the four sides and from the bottom of the mould and meeting in surfaces which are planes of weakness. The centre towards the top of the block is comparatively spongy, owing to imperfect agitation, and to the collection there of any impurities which the water may contain. To get the frozen ice out the moulds are lifted bodily, dipped into tepid water to thaw the surface, and tilted, so that the blocks slide out.

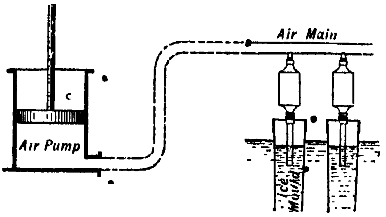

Fig. 41. Pneumatic Agitator.

Fig. 42 illustrates the cell system of ice-making. The tank containing the water to be frozen has a double bottom, and also an enclosure at one side, in which a plunger moves slowly up and down, forcing the water backwards and forwards through apertures in the upper bottom, into the spaces between the brine cells. The brine cells are long, narrow cases of wrought iron, with a series of wooden partitions extending horizontally across each, arranged so that the cold brine circulates in a zig-zag, and comes

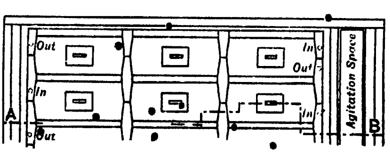

Fig. 42. Cell System of Ice-making.

in contact with every part of the surface of the cell. In the example shown here the brine cells have hollow projecting pieces on both sides, not only at the extremities, but also at the intermediate points, with the effect that the water space between one cell and the next is divided into three sections, completely enclosed within active brine walls. When the freezing is complete, and each section contains a solid block of ice, the circulation of cold brine is stopped, and tepid brine is passed into the cells to thaw off the blocks, which are then lifted out. In some applications of the cell system the hollow transverse projections from the cells are omitted, and the length of the water space is divided up by movable plates of metal, which serve to conduct heat away from the ends of the blocks. The blocks are usually about 12 in. thick, 2½ ft. or 3 ft. long, and 4 ft. high, and the freezing takes about 3 days.

In an earlier variety of cell system the brine cells were flat plates placed somewhat further apart, and ice was formed in slabs, which were not allowed to become thick enough to meet in the middle. Slab-ice admits of being particularly clear, but it has the drawback of taking a long time to make, since the heat is taken from one side only, and of being rather shapeless. The slab process has, however, been brought to great perfection in America, where it is used, for example, by Messrs Westinghouse and Kerr in the manufacture of what is there known as diamond-ice. The freezing surfaces in their plant are called dry-plates, and each consists of a gridiron of pipes in which ammonia is directly expanded. In some instances, the slab of ice is got off the dry-plate by passing warm ammonia gas through the pipes. In other cases, the slab is cut off by passing a steam cutter or knife with a thin hollow blade, served with live steam, between the dry-plate and the slab. The steam cutter also has transverse blades, which divide the slab into blocks of convenient size.

The preference which consumers generally feel for clear ice is mainly, if not wholly, sentimental. Opaque ice, or, as the Americans inauspiciously call it, from its resemblance to white marble, "tombstone-ice," is perfectly wholesome, provided, of course, the water used in making it is pure; on the other hand, the clearness of ice is no guarantee of the purity of the water. Opaque ice is cheap to make, and there seems no good reason why it should not be as acceptable as clear ice. Mr Lightfoot informs me that in the Linde factory at Hull, where 15 tons of opaque ice are made for each ton of coal burnt, the whole cost of the manufacture is a trifle under 2*s.* per ton, this figure including the cost of coal, the labour in stoking and attending the machinery, the wages of crane-men, the engine-house stores, such as oil and waste, and the loss of ammonia, as well as the cost of water. He uses an ordinary two-cylinder compound engine employing steam at 110 lbs. pressure. At Grimsby, where the Linde Company has put up another larger ice plant on the same general lines, he expects to get even better results, as he will there use triple expansion engines with steam at 160 lbs.

Ice Rinks.

An application to be mentioned before we leave the subject of ice making is the formation of ice rinks. The Linde Company put up an ice rink at Frankfurt as early as 1891, in which the brine pipe system was used, the pipes being placed in a shallow tray or cell of water, which was frozen bodily. Of the two public rinks in London[1], the one at "Niagara" has De la Vergne ammonia expansion plant, and the floor is made by a horizontal gridiron of brine pipes immersed in a tray containing water, the whole of which becomes frozen. At the National Skating Palace, Messrs Hall have a carbonic acid plant, with a floor made up of horizontal boxes or cells, through which brine is passed. The upper surfaces of these cells form a water-tight floor on which a comparatively shallow layer of water is frozen. The same advantage which this system possesses in having only a small volume of water to freeze, and in having a flat base below the water, is secured in another way in a rink which the Linde Company have put up at Nuremberg. There the floor is a shallow open tray, in which the water is frozen, resting on timbers which stand on a concrete floor below, and form channels through which a circulation of cold brine is maintained.

Dry Air Blast[2].

An interesting modern use of refrigeration is to cool air for the purpose of drying it, an effect which follows from the great reduction at low temperatures in capacity for holding moisture in suspension. (See Table in Appendix D, p. 187.) This treatment is now advocated, after successful trial in the Carnegie Steel Company's works near Pittsburg, for application to the air supplied to blast furnaces. It is claimed that drying the air results in a large saving of fuel and increase of output, and also in escaping variations in the quality of the iron, which are ascribed to the variable humidity of an ordinary air-blast, due to variations of atmospheric conditions. The air is cooled by passing through a chamber stacked with brine pipes, the coils being divided into sections, for the purpose of thawing off. The moisture is deposited on the pipes as water or as ice, the ice being periodically thawed off by passing steam-heated brine through the sections.

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[1] Both of these rinks have now (1908) ceased to exist.

[2] Added in 1908.

In a trial of this process air entering at an average temperature of about 75° Fahr. was cooled by passing through the brine-pipe chamber to 22° Fahr., and the amount of water held in it was thereby reduced from about 5·7 to 1·7 grains per cubic foot[1].

Cooling of the Magazines in War Ships[2].

Among small-scale applications of refrigerating plant an important one is to the magazines of war ships, where the object is to maintain a temperature low enough to prevent deterioration of the explosives. Without such cooling the magazines are liable in some cases to reach a temperature as high as 90° Fahr. through the unavoidable proximity of the magazine to boiler or steam-pipes, and even this may be exceeded if the ship is stationed in a warm climate. Such disasters as that which happened in 1907 to the French battle-ship *Jena* have been traced to the deterioration which nitrocellulose propellants suffer under such conditions. Protracted exposure to a high temperature brings about a gradual decomposition of their highly unstable constituents, which at an advanced stage produces so much evolution of heat as to cause the explosive to ignite spontaneously.

The propellants used in the British service, which are mixtures of nitrocellulose and nitroglycerine with a small proportion of mineral jelly, are considerably more stable, but even in their case continued storage at a temperature so high as 90° Fahr. would be dangerous, and steps are accordingly taken to reduce the temperature of ship's magazines to something like 60° or 70° Fahr., which is low enough to secure practically complete stability. For this purpose warships are now fitted with carbonic acid machines, these being considered safer for use in confined spaces, for the reasons that have been already stated. They are placed in compartments near the magazines, and are driven either electrically or by steam. They are employed to cool brine which is caused to circulate through one or more nests of cooling pipes, past which air from the magazine is caused to circulate. A single machine may, and generally does, serve more than one magazine, by being used to cool the brine for more than one nest of pipes. Each nest is placed above or close to a magazine, and short air trunks are led from the magazine to the cooling pipes and back, with a fan to maintain circulation of the air. The air trunks are extended throughout the magazine, with exhaust and delivery at various parts of the length, so as to secure that no part of the atmosphere of the magazine shall remain stagnant and warm. The use of brine pipes is preferred to direct expansion, as they are held to give greater facility in adjusting the amount of refrigerating effect in the various magazines which are served from one machine. The brine is not allowed to fall below 32° Fahr.—about 34° is the lower limit—and consequently no ice is formed on the brine pipes, though moisture is deposited. The chilled air before being discharged to the magazine deposits so much of its moisture on the pipes as to keep the atmosphere in the magazine relatively very dry, and a closed circulation is maintained, air being taken from the magazine, cooled, and returned to the magazine again.

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[1] See a paper on the application of dry-air blast to the manufacture of iron, by James Gayley, *American Iron and Steel Inst.* 1904.

[2] Added in 1908.

The arrangement as applied to the after magazines of a battleship is shown in Figs. 43 and 44. Fig. 43 is a plan of the magazine deck and Fig. 44 a plan of the deck above on which the air coolers are situated. The refrigerating machinery, consisting of the compressor and the brine pump, is placed in a compartment on the deck above that, above the position indicated at *A* in Fig. 44. The brine pipes lead from it to three air coolers, *B*, *B*, *B*, which serve the magazines immediately below. Each air cooler has 250 square feet of cooling surface. The construction of these coolers is shown by sectional views in Fig. 45. Each of them resembles a surface condenser; the cold brine circulates across the cooler through two groups of horizontal pipes, one group serving

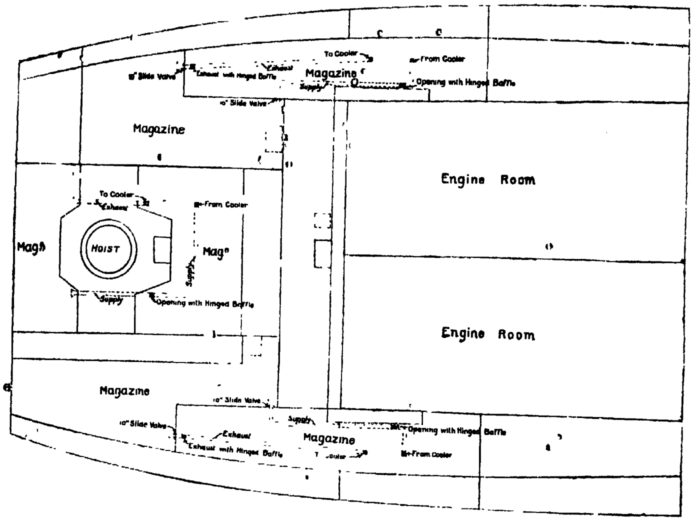

Fig. 43. Arrangements for cooling magazines on board ship.

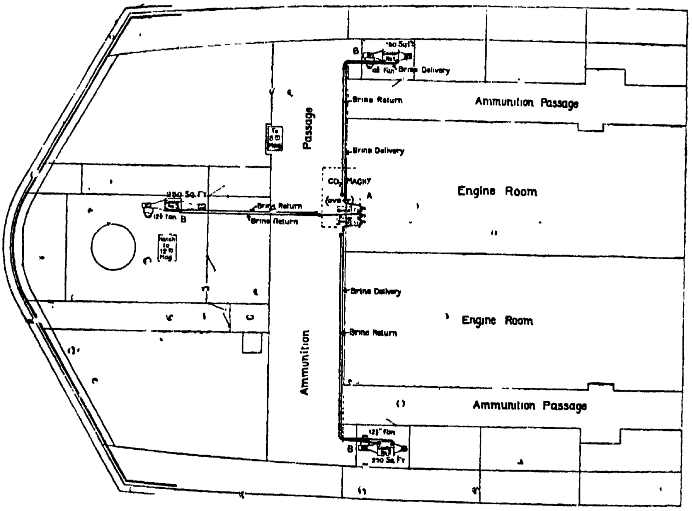

Fig. 44. Arrangements for cooling magazines on board ship.

as returns. The air passes longitudinally through the cooler and therefore at right angles to the pipes. To propel the air each cooler is fitted with an electrically driven 12½ inch fan. The air trunks are seen in Fig. 43. The exhaust air-trunk draws the air

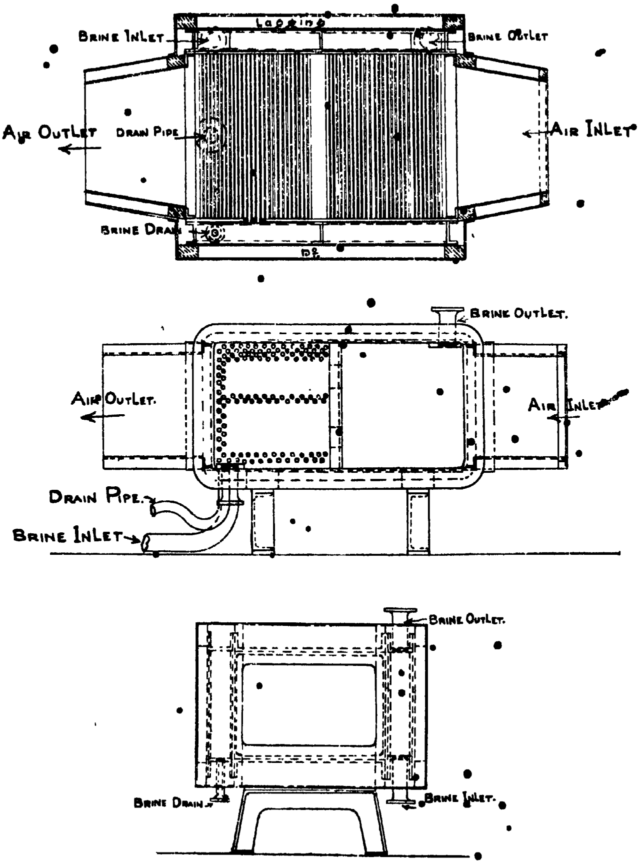

Fig. 45. Air cooler for cooling machines.

from the upper portion of each magazine, and then leads up to the cooler through the deck just where the cooler is situated. Similarly the air after being cooled is led directly down through the deck, and along a supply trunk which returns it to the magazines from which it came. The supply to each magazine is regulated by baffles or valves in the trunk.

The compressor in such cases is usually a carbonic acid machine of 50,000 thermal units capacity. Besides serving the air coolers it is arranged to be applicable to ice-making. For this purpose a small ice-making tank is placed in the compartment which contains the compressor, and valves are provided by means of which the brine circulation can be made to take place directly through this tank. In ice-making the brine is necessarily cooled to a much lower temperature than would do in the air-coolers, where we have to prevent the formation of ice on the pipes. Accordingly, while the apparatus is being used for making ice the magazine air coolers are shut off and the temperature of the brine is brought as low as may be desired. Fig. 46 shows diagrammatically the circulation of the brine in the two cases. When the

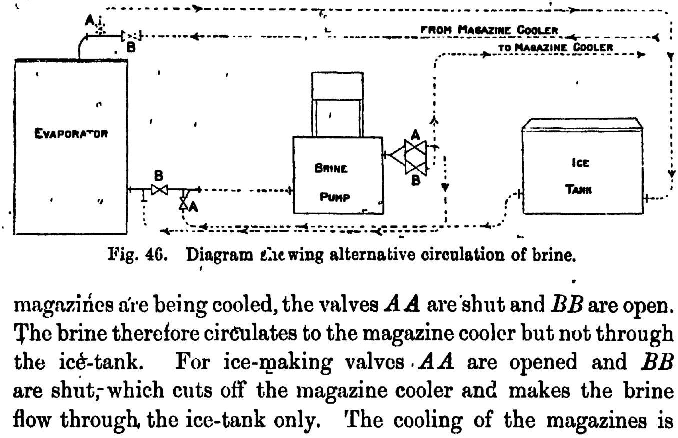

Fig. 46. Diagram showing alternative circulation of brine.

magazines are being cooled, the valves *AA* are shut and *BB* are open. The brine therefore circulates to the magazine cooler but not through the ice-tank. For ice-making valves *AA* are opened and *BB* are shut, which cuts off the magazine cooler and makes the brine flow through the ice-tank only. The cooling of the magazines is of course suspended while ice-making is going on.

Fig. 47 shows in plan a complete representative plant used in magazine cooling, which consists of a 50,000 British thermal unit carbonic acid compressor, driven in this example by a vertical steam engine. On the two sides of it are the condenser and evaporator consisting of precisely similar arrangements of pipe coils. Adjoining the condenser is the vertical steam-driven brine pump and on the other side the brine tank which contains three moulds for making in all 100 lbs. of ice at a time. Here again the valves

AAA are opened for ice-making and *BBB* are closed. The pipes *CC* lead to the air-coolers; when they are in operation the valves *BBB* are opened and *AAA* are closed.

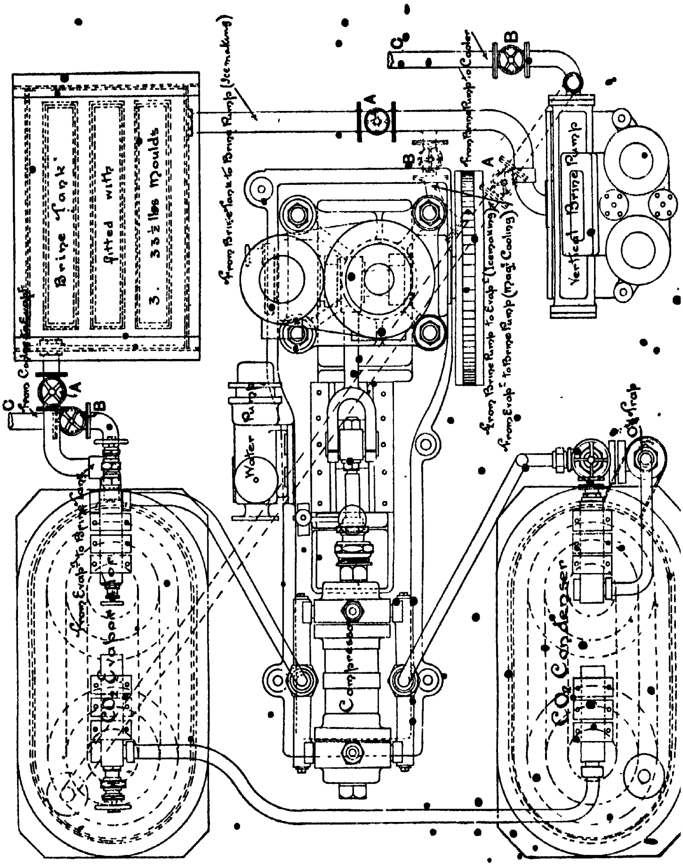

Fig. 47. Carbonic acid refrigerator used in cooling magazines.

LECTURE VI.

The Production of Very Low Temperatures.

IN none of the industrial uses already referred to is more than a moderate degree of refrigeration required. The temperature is rarely lower, and never many degrees lower, than the zero of the Fahrenheit scale. It is, however, the case that in some processes considerably lower temperatures are employed. Certain substances used in medicine are purified by crystallising them out under extreme cold. The rectification of chloroform for instance, and of nitrous oxide, is carried out by the use of low temperatures, and, to give a recent example of another kind, acetylene has been purified by subjecting it to a low temperature, and treating it with sulphuric acid. The acid is found not to act on the acetylene itself, when cooled to – 50° C., but to retain its action on the impurities which have to be removed. An easy means of getting low temperature (down to values of about – 80° C.) when small quantities of material have to be dealt with, is furnished by using compressed carbonic acid, allowing it to evaporate freely in the air, when it reaches a temperature approaching that limit. Apart from commercial uses the production of very low temperatures is a problem of great physical importance, interesting alike in itself and in its results. Quite recently great strides have been made in this subject. It is now an easy matter to produce the extreme degrees of cold necessary to liquefy oxygen and air, and it is not unlikely that the liquefaction of air will soon take its place among ordinary industrial operations[1]. In order to liquefy any gas, the temperature must be reduced below its critical point, otherwise no amount of pressure, however great, will make the gas change its state. We may define the critical temperature of a gas as the highest temperature at which it can exist in the liquid form under any pressure whatever.

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[1] The paragraphs added at the end of the Lecture will show that this expectation has been realized (1908).

Liquefaction of Gases by Cailletet and Pictet.

The attention of the scientific world was arrested in the beginning of the year 1878 by the news which reached it almost simultaneously from two sources, that two independent experimentalists had succeeded in liquefying certain of the so-called permanent gases which had been left unliquefied in the earlier experiments of Faraday. Cailletet and Pictet, within a few days of one another, but independently, and by more or less distinct methods, succeeded in liquefying oxygen, nitrogen, and other gases. Pictet employed what we may distinguish as the cascade or successive cycle method. The general idea of this method is illustrated in Fig. 48. Imagine a refrigerating agent, such as carbonic acid, to have been compressed and to expand through a valve into the chamber, A, where it evaporates. In the example as sketched it is escaping from A to the atmosphere. When carbonic acid evaporates freely to the atmosphere it falls to a temperature of about $-80°$ C. It could be made to go 30

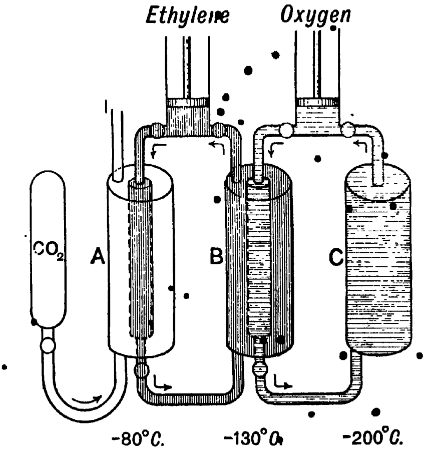

Fig. 48. Cascade Method of reaching very Low Temperat

degrees or more lower by using an air-pump to preserve a partial vacuum in the chamber; but, assuming the pressure in *A* to be atmospheric, the temperature then will be about − 80° C. Now we may use this as the condensing temperature of some other more volatile material. The material which is indicated in the sketch is ethylene, which was not used by Pictet, but has come into use subsequently, and has done good service in the hands especially of Professor Dewar. It forms a convenient intermediate link between the comparatively easily liquefiable carbonic acid and the much more difficult oxygen. Ethylene has a critical temperature of − 10° C. and needs only moderate pressure to liquefy it when exposed to a temperature of − 80° C. It is pumped at the necessary pressure into the inner vessel at *A* and is there liquefied and passes through an expansion valve to the outer vessel at *B*, where it evaporates. The pressure in *B* is supposed to be kept at something not much over one inch of mercury, and in that case the temperature reached by the ethylene in evaporating will be − 130° C. After expansion it is re-compressed, so that the part of the apparatus in which the ethylene is carried through its cycle may simply be regarded as a separate vapour compression refrigerating machine, the same in kind as the ordinary machine using ammonia or carbonic acid, but with ethylene as its working substance, and with *B* as refrigerator and *A* as condenser.

The remainder of the apparatus is another similar machine, using, in this case, oxygen as its working substance, and with *B* as its condenser. The critical temperature of oxygen is about − 118° C., and, as the temperature in *B* is lower than that, the oxygen liquefies when compressed into the inner vessel at *B*. A moderate pressure of 20 or 30 atmospheres suffices. The liquid oxygen may be passed through a valve, and evaporated again in the vessel *C*, and in that way a temperature of − 200° C., or lower, can be reached, the temperature, of course, in this last vessel depending on the pressure in it, and, consequently, on the rapidity with which the pump is worked. By working the pump tolerably fast, to preserve a good vacuum in *C*, we can get down to something like − 220° C., or even − 225° C., a temperature which is no very long way above the absolute zero − 273° C. In Pictet's cascade of successive cycles, the substances used were sulphurous acid and carbonic acid. The ethylene is a useful addition, as giving readily a temperature considerably below the critical point of oxygen. Without it, however, Pictet succeeded in liquefying oxygen by the device of letting it suddenly escape when under high pressure and after being cooled as far as the carbonic acid would cool it, though the temperature reached while the gas was under compression was considerably short of the critical point.

Cailletet did not use the method of the cascade. He compressed the gas under very high pressure, and cooled it moderately, so that it was still far above its critical temperature. He then allowed it suddenly to expand by opening a tap, which relieved the pressure on the gas. In expanding it did work against a column of mercury which was used in his apparatus as the equivalent of a piston for compressing the gas. The gas, therefore, cooled itself, the expansion being sudden and nearly adiabatic. This reduced the temperature below the critical point, while the pressure was still left high enough to liquefy the gas at the temperature which it had then acquired. The chamber containing the gas was of glass, and the liquefaction became apparent by the formation of a mist.

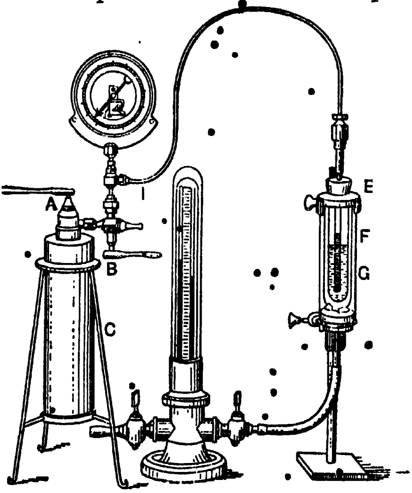

Fig. 49.

Fig. 49, which is copied from a paper by Professor Dewar[1], shows an improved apparatus based partly on Pictet's method and partly on Cailletet's. An iron flask, *C*, contains highly compressed oxygen or air, or whatever gas is to be treated. The gas passes from this flask, through a small pipe, *I*, into the inner tube at *F*. This tube is surrounded by a vessel, *G*, containing some other substance more easily liquefied than the gas in the inner tube. Suppose, for example, that *G* contains carbonic acid. An orifice, *E*, near the top leads, by an annular passage round it, into an outer chamber, from which the gas is drawn away by an air pump. This keeps the temperature in *G* considerably below −80° C., and if a good vacuum is maintained it may be as low as −115° C. Say that compressed oxygen is coming into the tube *F*: the critical temperature of oxygen is a trifle lower than this, and hence, under these conditions, the oxygen will just fail to liquefy. But let the stopcock *A* be closed, and the other, *B*, suddenly opened to allow the pressure in *F* to be reduced; immediately a portion of the oxygen will condense. The adiabatic expansion which occurs in the sudden release of part of the gas causes what is left to fall to a temperature below its critical point. Instead of using carbonic acid in the jacket, *G*, Professor Dewar preferred to use liquid ethylene. Ethylene readily evaporates at a temperature below the critical point of oxygen, consequently, without using the sudden expansion which was the characteristic feature of Cailletet's method, the oxygen can then be condensed under steady pressure in the inner tube.

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[1] *Phil. Mag.*, Sept., 1894.

Subsequent Work by Dewar and others.

Two years later Professor Dewar decanted liquid oxygen into an open glass vessel from a spiral worm of copper tube, in which it was liquefied under pressure, the worm being cooled by enclosing it in a chamber from which liquid ethylene was evaporated. A tap at the bottom of the worm could be closed to allow the liquid oxygen to accumulate, and opened to let it pass into an open test-tube, which was kept cool by a jacket of evaporating ethylene in order to prevent the liquid oxygen from evaporating too rapidly. The ethylene was liquefied by compressing it in another worm surrounded by carbonic acid snow. His apparatus is shown in Fig. 50[1]. An interesting feature in this, as well as in the apparatus of Fig. 49, is that the liquid ethylene is, to a great extent, protected from conduction of heat into it by a jacket through which the vapour circulates which is given off by the ethylene itself. A similar arrangement for the decanting of condensed oxygen was used in 1890 by Professor Olszewski[1], who has been assiduous in the same field of research. Other names which should be mentioned in this connection are those of the late Professor Wroblewski, Professor Witkowski, and Professor Onnes, of Leyden.

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[1] See *Proc. Roy. Inst.*, June, 1886, and *Phil. Mag.*, March, 1895.

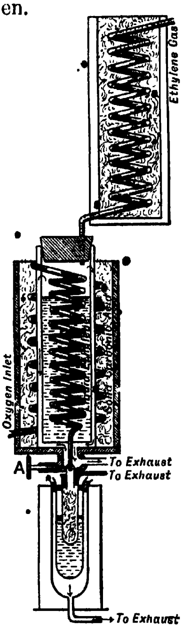

Fig. 50.

It would be beyond the scope of these lectures to refer in detail to the large amount of work which has been done in investigating the properties of matter at extremely low temperatures or to make any attempt at apportioning credit to the various workers, whose claims have in some cases been discussed with a degree of warmth scarcely appropriate to the subject. With liquid oxygen or liquid air available as a laboratory agent new fields of research have become open. It is now possible and even easy to examine the mechanical, electrical, and magnetic qualities of substances under conditions previously unattainable.

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[1] *Phil. Mag.*, Feb. 1895.

partly on Cailletet's. An iron flask, *C*, contains highly compressed oxygen or air, or whatever gas is to be treated. The gas passes from this flask, through a small pipe, *I*, into the inner tube at *F*. This tube is surrounded by a vessel, *G*, containing some other substance more easily liquefied than the gas in the inner tube. Suppose, for example, that *G* contains carbonic acid. An orifice, *E*, near the top leads, by an annular passage round it, into an outer chamber, from which the gas is drawn away by an air pump. This keeps the temperature in *G* considerably below −80° C., and if a good vacuum is maintained it may be as low as −115° C. Say that compressed oxygen is coming into the tube *F*: the critical temperature of oxygen is a trifle lower than this, and hence, under these conditions, the oxygen will just fail to liquefy. But let the stopcock *A* be closed, and the other, *B*, suddenly opened to allow the pressure in *F* to be reduced; immediately a portion of the oxygen will condense. The adiabatic expansion which occurs in the sudden release of part of the gas causes what is left to fall to a temperature below its critical point. Instead of using carbonic acid in the jacket, *G*, Professor Dewar preferred to use liquid ethylene. Ethylene readily evaporates at a temperature below the critical point of oxygen, consequently, without using the sudden expansion which was the characteristic feature of Cailletet's method, the oxygen can then be condensed under steady pressure in the inner tube.

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[1] See *Proc. Roy. Inst.*, June, 1886, and *Phil. Mag.*, March, 1895.

Dewar's admirable device of the open vacuum-jacketed vessel enables liquid air and other liquefied gases to be decanted and handled with the greatest ease, to be conveyed from place to place, and to be stored for short periods with no more than a moderate loss by evaporation. It is an appliance of first-rate importance in researches at extremely low temperatures.

Regenerative Method of Producing Very Low Temperatures.

The production of very low temperatures has in recent years received a novel and highly interesting development through an application of the regenerative principle. In speaking of machines which produce refrigeration by the expansion of air, I drew attention to the early suggestion by Siemens of the use of a regenerator or counter-current heat interchanger, and we saw that the regenerative principle again found application in the hands of Kirk.

Siemens, in his patent of 1857, describes the employment of an interchanger to extract cold from the air already cooled by a refrigerating machine, and thereby to cool the air which is on its way to being expanded. He pointed out that in theory at least there was no limit to the degree of cold which could be produced by the application of this interchanger. His provisional specification, which was never completed, gives an example of the temperatures that might be expected in a particular case, and proceeds:—"These temperatures are mentioned, not as absolute temperatures, but to show that the principle of the invention is adapted to produce an accumulated effect, or an indefinite reduction of temperature."

Siemens' idea was that the compressed air should pass through this interchanger, and should then be caused to do work in an expansion cylinder. This expansion would chill it, and it would then pass again through the interchanger, giving up its cold through the interchanger to the next succeeding supply of compressed air. The effect would be to make each fresh supply, on its way to the expansion cylinder, a little colder than the last. A cumulative fall in temperature would result which would only be limited by accidental losses due to conduction of heat from outside and to heat developed from friction within the machine.

It does not appear that Siemens followed up his idea. In 1885, Solvay patented an apparatus and process for producing, applying, and keeping up extreme temperatures. It was a regenerative method somewhat resembling that of Siemens, but with a regenerator instead of an interchanger. Solvay constructed an apparatus, by which he was able to reach a temperature of about −95° C.[1] He found that at that temperature the losses of cold balanced the gains. In 1892, Windhausen also patented an apparatus for producing extreme degrees of cold, in which an interchanger essentially like that of Siemens was used in combination with an expansion cylinder.

Mr Windhausen tells me that this invention is now in use on a commercial scale for such processes as the extraction of benzol from the mixed gases which are given off by the distillation of coal. The industrial application which he had in his mind was the separation of such volatile constituents of mixed gases, by fractional distillation at low temperatures. He tells me that about 50,000 cubic metres of the mixed gases given off from coal are treated daily under a pressure of 2 to 2½ atmospheres, the temperature reached being about −90° C., or −95° C. (the same temperature as Solvay reached), and at this temperature 20 to 30 grammes of benzol are got from each cubic metre of the gas, the remainder, namely about 98 per cent., passing off as gas to be used in the ordinary way.

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[1] *Comptes Rendus*, Dec., 1895.

The Step-down in Temperature.

To make the interchanger of any use in causing a cumulative fall in temperature the gas passing out through it must have suffered a step-down from the temperature it took in coming in. In the inventions of Siemens, Solvay, and Windhausen, this step-down is produced by causing the gas to do work in an expansion cylinder. The step-down is essential to a cumulative cooling, but it may be caused to happen in more than one way. There are, in fact, two ways by which that step-down in temperature may be produced. One is the way these inventors have used, namely, to make the gas do work, say against a piston in an expansion cylinder. But there is another way without the use of an expansion cylinder at all, namely, by merely letting the gas stream through a constricted aperture or throttle-valve. The gas then expands without doing work; it consequently becomes much less cooled than when it does work in an expansion cylinder, but it becomes cooled to a certain small extent. In early experiments by Joule, where a gas moderately compressed and brought to atmospheric temperature was allowed to expand through a throttle-valve from one vessel to another, he did not observe cooling, and he drew the conclusion that the internal energy of a gas does not depend upon its pressure, but only on its temperature, which is given in text-books as Joule's law. But later experiments by Joule himself in conjunction with Thomson (Lord Kelvin), showed that this law was not exactly true of real gases, though it is convenient to retain it as an expression of what would be true of an imaginary substance called a "perfect gas." All real gases are more or less imperfect, in the sense that their physical behaviour deviates, more or less, from the simple laws which hold for a perfect gas. By forcing air and other gases through porous plugs serving as constricted apertures Kelvin and Joule established the fact that there is some cooling when they expand without doing work. The amount of this cooling, which is called the Joule-Thomson effect, is, in general, very small, and that is why an ordinary air refrigerating machine cannot operate without having an expansion cylinder as well as a compression cylinder. It would not produce any refrigeration worth speaking of if a regulating throttle-valve such as serves in an ammonia-machine were substituted for the expansion cylinder, when we are dealing with air as the working substance in a refrigerating machine of the Bell-Coleman type. In a vapour compression machine the regulating valve does serve as an effective substitute for the expansion cylinder because condensed vapour cools itself very much in passing through such a valve. Even in a carbonic acid machine in the tropics, where the compressed vapour is at a temperature above its critical point and is therefore not condensed, expansion through the regulating valve is still effective in cooling the gas, because the gas in this condition is very far from being a perfect gas and does not even approximately conform to Joule's law. But with air, or with any of the so-called permanent gases, the deviation from Joule's law is small, and the extent to which the temperature falls when compressed air streams through a throttle-valve is only about one quarter of a degree on the Centigrade scale for each atmosphere by which the pressure drops. This is when the air is at anything like ordinary atmospheric temperature; but if it is very cold to begin with, the fall in temperature is greater, for it is then a less perfect gas and deviates more widely from Joule's law[1].

Application of the Regenerative Method.

Suppose now that air compressed to a pressure say of 100 atmospheres is made to pass through a long coil of pipe and to escape at the end through a small nozzle. Its temperature drops at once by something like 25 degrees Centigrade. Let the gas which is

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[1] Kelvin and Joule found there was cooling in all the gases they tested except hydrogen, which actually became hotter when forced through the constricted aperture or porous plug. It is now known that hydrogen is cooled, like other gases, provided the initial temperature is below a certain limit. For any gas there is in fact a particular temperature below which the effect of throttling is to cool the gas, and above which the effect of throttling is to heat it. In hydrogen this temperature is comparatively low. The cooling effect in any gas is augmented the further the actual temperature is below the limit at which the inversion of effect takes place. In hydrogen, at the temperature of liquid air, the fall is about one quarter of a degree per atmosphere. In air, according to Kelvin and Joule's experiments, the fall in degrees Centigrade is given by the expression

$$0{\cdot}276\,(p_1 - p_2)\left(\frac{273}{T}\right)^2,$$

where p_1 and p_2 are the pressures, in atmospheres, before and after the throttling, and T is the absolute temperature before throttling.

cooled by this drop escape through an interchanger, in close contact with the coil of pipe, so that it gives up its cold to the gas which is on its way to the nozzle. This produces a preliminary cooling of the gas that is not yet expanded; its expansion through the nozzle then cools it further, and after that it passes away through the interchanger to effect a still further cooling of the incoming gas. The process goes on cumulatively, and the temperature in the pipe and at the nozzle falls without limit, or rather until a limit is reached which is determined by the leakage in of heat from outside, and by the imperfection of the interchanging process.

But if care be taken to insulate the apparatus well, and make the interchanger so efficient that the temperature of the gas as it finally escapes is only very little lower than the temperature of the compressed gas that is entering the pipe, an exceedingly low level of temperature may be reached at the nozzle, a temperature indeed so low that the air which issues from the nozzle will be in a liquid state. The early stages may be abbreviated if the compressed gas is cooled to some extent beforehand by other means as, for instance, by passing it through a pipe surrounded with carbonic acid snow. Such precooling will not only make liquefaction begin sooner but will increase the proportion of gas that is liquefied when the working of the apparatus has reached a steady state.

There are two essential factors in this regenerative method of producing extreme cold, namely (1) the drop in temperature on expansion, and (2) the interchange of heat by which the air which has already suffered that drop cools the air that has yet to be expanded. The drop in temperature may, as we have seen, be produced by expansion under such conditions that the air does work, instead of by expansion through a nozzle, when it does not. Expansion doing work would be theoretically better, inasmuch as it would yield a much larger drop: but practically expansion through a nozzle has so far been found to be best when extremely low temperatures are aimed at. The use of a piston and cylinder at temperatures such as that of liquid air would involve formidable difficulties in the way of lubrication as well as of thermal insulation, and much the same objection would apply to a turbine, which has been thought of as an alternative means of augmenting the drop by giving the expanding air work to do. A nozzle is easily insulated from its surroundings. An expansion cylinder is not only harder to insulate, but will have heat generated within it by friction. Solvay, using an expansion cylinder to cause the drop, found that the lowest temperature he could reach was -95° C.; beyond this point the losses were in excess of the cold produced. But a temperature of -200° C., or even lower, is reached without difficulty, when instead of an expansion cylinder, a throttling nozzle is used to cause the drop.

This principle of regenerative cooling was first successfully employed by Linde for the production of extremely low temperatures, and for the liquefaction of air. In the summer of 1893 he invented an apparatus, shown diagrammatically in Fig. 51. It consists of an interchanger, *C D E*, formed of two spiral coils or worms of pipes, one inside the other. A compressing pump *P* delivers air under high pressure through the valve, *H*, into a cooler, *J*, where the heat developed by compression is removed by water circulating in the ordinary way from an inlet at *K* to an outlet at *L*. The highly compressed air then passes on through the pipe *BC* to the inner worm, and after passing through the coils, *D E*, expands through the throttle-valve, *R*, into the vessel *T*, thereby suffering a drop in temperature. Then it returns through the outer worm, *F*, and, being in close contact with the inner worm, gives up its cold to the gas that is still on its way to expand. Finally it reaches the compression cylinder, *P*, through the suction valve, *G*, and is compressed to go again through the cycle. The tap, *V*, allows the liquid gas to be drawn off, and this loss is made good by pumping in more air through the stop-valve at *A*.

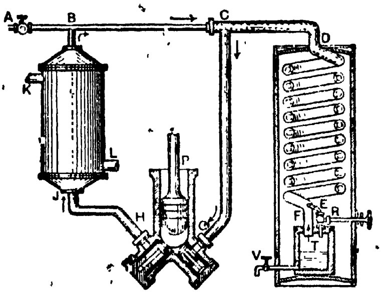

Fig. 51. Linde's Regenerative Apparatus.

Linde used no preliminary cooling of the air. Starting with everything at atmospheric temperature, he succeeded, in May, 1895, after some 15 hours of continuous operation, in producing so great an accumulated effect that liquid air began to run out of the nozzle. He patented the process in June of that year, and the earliest account of his work published in English appeared in October in the *Engineer*[1]. The novelty and excellence of Linde's invention lie in the combination of the regenerative interchanger with the expansion nozzle as a means of producing what I have called the drop. The regenerative principle had been employed before to accumulate the cooling effect of expansion in a cylinder, but no one had used it to accumulate the small effect which had been exhibited by the experiments of Kelvin and Joule.

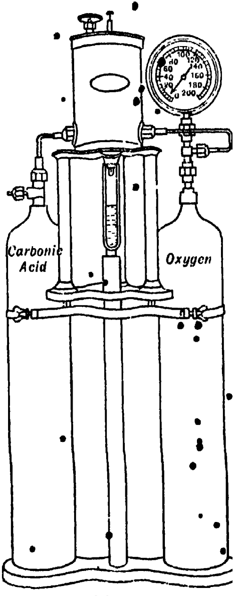

Fig. 52.

More recently the same method has been employed by Dewar, and has led, in his hands, to the construction of a remarkably simple laboratory apparatus for liquefying oxygen or air. A general view of the apparatus is shown in Fig. 52 and a section in

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[1] See also the *Engineer* of November 13 and 20, 1896.

Fig. 53. One flask contains the oxygen, compressed to a pressure of about 150 atmospheres, the other contains compressed carbonic acid. The oxygen passes through a long spiral of small copper pipe. It is in the first place cooled by carbonic acid released from the other flask. This preliminary cooling is used to accelerate the action. Linde showed that it was possible to start with air at the atmospheric temperature, and to get it cooled down below the critical point and ultimately liquefied. But by using carbonic acid to cool the air beforehand to − 80° C. or so, the action is much hastened, and in about five minutes we find liquid oxygen streaming from the nozzle into

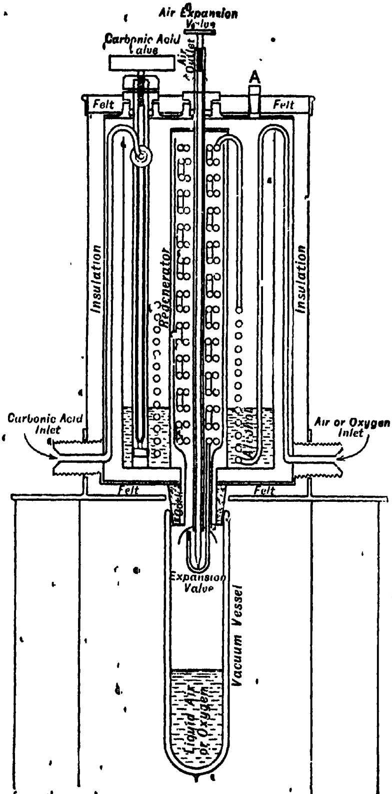

Fig. 53.

the vacuum vessel placed there to receive it. Owing to the presence of slight impurities, it is a turbid-looking liquid, but when we pass it through a filter paper into another vacuum vessel it becomes clear and shows the pale blue tint characteristic of liquid oxygen. Following Professor Dewar, we may demonstrate some of its properties. That it is giving off oxygen vapour is shown by dipping a glowing match into the top of the vessel: the match immediately bursts into flame. A spiral of lead wire dipped into the liquid becomes so elastic under the extreme cold that a weight hung from it will dance up and down as it would if the wire were of steel. But as the lead spiral recovers its usual temperature by taking in heat from the air of the room its elasticity disappears, and the weight, which it bore easily when cold, begins to draw it out and finally pulls it nearly straight. Another effect of the cold is shown by dipping a sponge into the oxygen and applying it to the back of a piece of paper coloured with cinnabar: the pink colour of the cinnabar disappears. Another is shown by applying liquid oxygen to some spot on the outside of a flask full of bromine vapour. The flask loses its orange colour, for the vapour has condensed, forming a solid deposit on the glass at the place that has been chilled. An india-rubber ball dipped into the liquid oxygen becomes so brittle that when it is thrown against the wall it breaks into fragments, and a piece of rubber tubing similarly chilled snaps like a rod of glass when we attempt to bend it. Organic substances such as an egg-shell or an ivory paper-knife, when cooled by liquid oxygen, and then exposed to the strong light of the electric arc, show phosphorescence in the dark. A magnet is strengthened by the extreme cold, as the molecular theory would lead us to expect. The magnetic and electric qualities of matter at low temperature have lately been the subject of extended study by Professors Fleming and Dewar.

It is a curious coincidence in the history of invention that some four or five weeks before Dr Linde applied for his English patent an application accompanied by a provisional specification was filed on 23 May, 1895, by Mr William Hampson, for "Improvements relating to the progressive refrigeration of gases." The text of this provisional specification was brief, and may be quoted in full:—"The usual cycle of compressing cooling and expansion is modified by using all the gas, after its expansion, to reduce as nearly as possible to its own temperature the compressed gas which is on its way to be expanded; with this object all the expanded gas surrounds the pipe or pipes of compressed gas through all their length from the point of expansion to the point of normal temperature, and the length of pipe is sufficient to allow of the fullest possible interchange of temperatures between the compressed and expanded gas."

It is by no means easy to say how much credit should be assigned to this publication. Does "the usual cycle of compressing, cooling, and expansion" mean a cycle in which expansion is performed in a cylinder, as it is in ordinary air machines, or by passing through a throttle-valve, as in machines which use ammonia or sulphurous acid or carbonic acid? Mr Hampson was endeavouring to get his ideas brought to a practical issue for some years before the date of his application, but he had made no apparatus. Meanwhile, Dr Linde's invention was produced, complete, and in a form that demonstrated its practicability. Whatever credit belongs to Mr Hampson takes nothing from that which is due to Dr Linde. Since then, Mr Hampson has made experiments at Brin's Oxygen Works, and he informs me that with only 90 or 100 atmospheres of pressure he has got liquid air in three-quarters of an hour without any preliminary or auxiliary refrigeration.

In Linde's first apparatus the interchanger was made of iron pipes, with internal diameters exceeding 1 and 2 inches respectively, and weighing, with the collector and its fittings, fully one and a quarter tons. It was the large mass of the apparatus that made the period of cooling take as long as 15 hours, but once liquid air began to be formed, more than half a gallon (3 litres) was got per hour. With a smaller apparatus weighing half a ton, and with higher pressure, the period of cooling was reduced to five hours. In that case the air to be liquefied was distinct from the air which circulated through the tubes. It was pumped under a pressure of three atmospheres into a separate closed vessel placed within the chamber into which the nozzle of the interchanger opens. In a third experiment, Linde used copper tubes weighing 130 lbs., and reduced the period of cooling to two hours, one-fifth of a gallon of liquid air being then obtained per hour. We have seen that by the use of lighter apparatus, with the aid of auxiliary cooling by carbonic acid, small quantities of liquid air may be got in a still shorter time.

In cooling a gas by making it expand through a constricted orifice, the amount by which the temperature drops is proportional to the difference of the pressures p_2 and p_1 on the two sides of the orifice. But the work which the pump has to do in forcing the air to pass again and again round the cycle depends not on the difference but on the ratio of p_2 and p_1. Hence, to make the system efficient, what is aimed at is a large difference $p_2—p_1$, but a small ratio $\frac{p_2}{p_1}$. This requires that p_2 should be high, and p_1 moderately high. Dr Linde accordingly makes the upper limit of pressure, p_2, about 200 atmospheres, and in some cases he makes the pressure on the other side of the orifice as much as 50 atmospheres. Thus a drop of 150 atmospheres is then associated with the very moderate value of four for the ratio p_2 to p_1. On the other hand, if in passing the orifice the pressure of the gas were allowed to fall to that of the atmosphere, the drop on which the cooling effect depends would be increased from 150 to 199, but the ratio on which the work depends would be increased from 4 to 200. The cooling effect would be only one-third greater, whereas the work to be done by the pump, which varies as the logarithm of this ratio, would be nearly four times as great in the second case as in the first. The efficiency of the process is therefore nearly three times greater in the first case.

Even after the apparatus has become fully cooled down, and has attained a uniform regime in its working, only a small portion of the air that passes through the orifice is liquefied; the greater part returns to the pump to be compressed and sent through the orifice again. Hence it is important to maintain a comparatively high back pressure, p_1, for the greater part of the gas, and only to allow the portion that is to be withdrawn from the apparatus to fall to atmospheric pressure. This is done in a more recent apparatus by Dr Linde, in the manner shown in Fig. 54, which illustrates a laboratory form[1].

There are two throttle-valves, *a* and *b*. All the compressed air passes through *a*, but only a small proportion (about one-fifth) passes also through *b*. The passage through *a* causes a drop in pressure from 200 atmospheres to 16 atmospheres, and four-fifths of the air in circulation passes back at that pressure through the middle one of the three tubes composing the interchanger to the pump *d*. The remaining fifth passes through *b*, and about one-fourth of it gathers as liquid in the vacuum-jacketed vessel *C* at a pressure which is only so much above that of the atmosphere as will allow the liquid to pass out when the stop-cock *h* is opened.

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[1] Exhibited at the Society of Arts, March, 1898 (*Jour. Soc. Arts*, March 11, 1898).

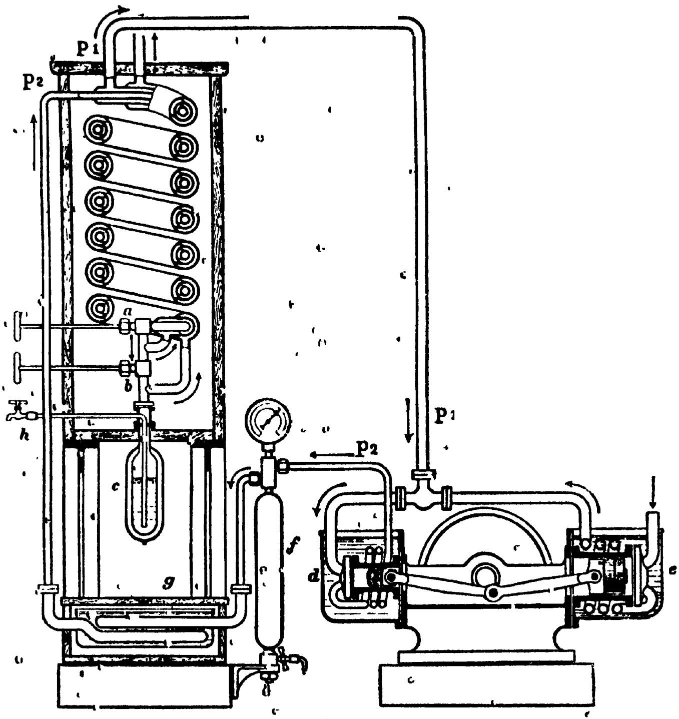

Fig. 54.

The unliquefied or re-evaporated part of what has passed through *b* escapes through the outermost tube of the interchanger. The pump *e* takes in fresh air from the atmosphere, compresses it to 16 atmospheres' pressure, and delivers it so that it mixes with the air which is returning at that pressure from the middle tube of the interchanger to the pump *d*. The pump *d* delivers air at 200 atmospheres to the innermost tube of the interchanger through which it passes to the throttle valves. The compressed air, on leaving each pump, passes through a coil in a water-cooler which also serves to jacket the pump. A small quantity of water is drawn in along with the air by the low-pressure pump; and this, together with the natural moisture of the air, is extracted as completely as possible, first by means of a separator *f*, and then by making the compressed air pass through a coil *g* in a bath of ice and salt before it goes into the interchanger. The interchanger is enclosed in a case packed with sheep's wool.

The machine circulates about 15 cubic metres of air per hour in the circuit from 200 atmospheres to 16 atmospheres. About three cubic metres per hour are pumped in from outside, and this is the amount which passes through the lower valve. About 0·9 litre of liquid air are formed per hour, with a continuous expenditure of three horse-power.

Application of the Method to Extract Oxygen from Air.

The first application of Linde's invention as a means of separating the oxygen from the nitrogen of air was made by Linde himself, and is included in his patent of June, 1895. The principle is that when air is liquefied, the nitrogen, being rather the more volatile constituent, tends to evaporate first. Its boiling point is only about 13° below that of oxygen, but this difference is enough to cause the liquid air that is left in the vacuum vessel to become richer and richer in oxygen as the process of evaporation goes on. By letting a considerable part of the liquid evaporate a liquid residue is left which consists largely of oxygen. Hence in the later stages of the evaporation an atmosphere is given off in which the proportion of oxygen is relatively large. Linde's object is to obtain, for commercial uses, such an atmosphere. He effects this by dividing the interchanger into two parts, down which the compressed air streams in parallel (Fig. 55) through the two inner pipes, which converge at *A*. The compressed air goes on through a worm in the receiver, *B*, passes the throttle-valve, *C*, and is delivered into *B* in a liquid state. From the surface of the liquid in *B*, nitrogen (mainly) evaporates, its evaporation being stimulated by the worm in *B*, and this passes off through one of the two interchangers, going out at *N*. The liquid in *B* becomes rich in oxygen, and this is allowed to pass slowly through the throttle-valve, *D*, into the outer coil of the other interchanger, where it evaporates, gives up its cold to the incoming air, and passes out at *O*. The gas drawn from *O* consists largely of oxygen. The supply of compressed air to the two parts of the coil is regulated by two stopcocks at the top, so that the escaping gases have the same temperature, and care is taken to make that temperature only a few degrees lower than the temperature at which the compressed air goes in. Notice in this device the important function discharged by the worm in *B*. It enables the latent heat required for the evaporation of the liquid to be extracted from the incoming compressed air, which thereby becomes, in fact, liquefied. This is an extension of the regenerative principle and leads to a great economy of power. We may say that the principle of interchange is here applied to the latent heat of liquefaction as well as to the heat that is given out in cooling the gas to the temperature at which liquefaction takes place.

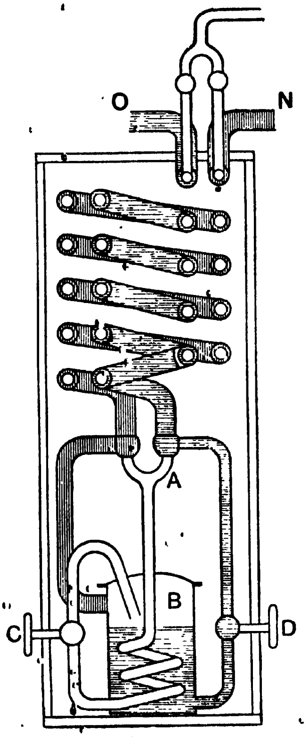

Fig. 55.

The separation of the two gases is by no means complete, but by allowing a rather large proportion of the whole liquefied air to escape through N by evaporation from the surface it is practicable to get from the O tube a gas containing some 50 or 60 per cent. of oxygen.

Dr Linde has given me the following figures, deduced from his own experiments, which show how the constitution of the liquid changes during slow evaporation. In the Table m is the percentage of the whole liquid which remains at each stage in the evaporation; a is the percentage of oxygen in it; b is the percentage of oxygen in the vapour then coming off, and n is the percentage of the original quantity of oxygen which still remains in the liquid.

m Per cent. of liquid not yet evaporated	a Per cent. of oxygen in liquid	b Per cent. of oxygen in vapour coming off	n Per cent. of original oxygen still in liquid
100	23·1	7·5	100
50	37·5	15	80
30	50	23	65
20	60	34	52
15	67·5	42	43
10	77	52	33
5	88	70	19

These results are also given in the curves of Fig. 56.

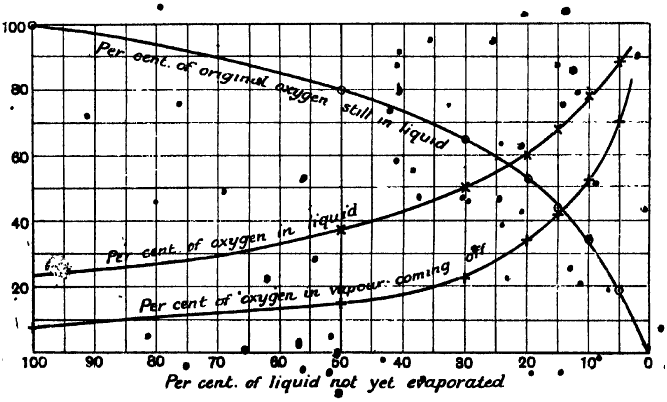

Fig. 56.

Thus, for example, by the time 70 per cent. of the liquid has disappeared in quiet evaporation, the remainder (viz., 30 per cent.) contains 50 per cent. of oxygen. The gas then coming off contains 23 per cent. of oxygen. And out of the whole quantity of oxygen which was present in the original liquid 65 per cent. is still there. I understand these figures were obtained by examining the proportion present in the gas given off at each stage: in other words, the points in the curve *b* were found by experiment, and the other quantities were deduced by calculation from these.

It is only when evaporation is going on very quietly that these results hold good. Anything like violent boiling has the effect of carrying off the oxygen more rapidly, and consequently of preventing, to some extent, the enrichment of the residual liquid. When this method of separating oxygen from nitrogen is carried out on a commercial scale, the evaporation cannot well take place so quietly as it took place in these experiments. Dr Linde tells me that when working under practical conditions he has to allow about four-fifths of the liquid to evaporate in order that the residue shall contain 50 per cent. of oxygen. Even then, however, some 40 to 45 per cent. of the original oxygen remains in the unevaporated liquid[1].

Laboratory form of Interchanger. Liquefaction of Hydrogen by Dewar.

Fig. 57 illustrates one of the simplest forms in which the heat interchanger has been arranged by Professor Dewar for laboratory work on a small scale. A single spiral of copper pipe, *BA*, fits closely into a vacuum vessel, and another vessel in the form of a closed tube from which the air has been extracted fits closely into the spiral. The annular space between the two is formed into a helix by the spires of the copper tube, and up this helix the expanded gases pass after issuing from the nozzle at the bottom of the tube. The vacuum vessels shelter the coil against conduction of heat either from outside or from the middle space.

Fig. 58 shows the arrangement used by Professor Dewar to get a jet of liquid hydrogen. The hydrogen, highly compressed in the flask *A*, passes first through a coil cooled by carbonic acid snow in *B*, then through another cooled by liquid ethylene in *C*, and goes on to the third vacuum vessel *D*, which contains a long coil serving as an interchanger. It expands at the bottom of this coil, *G*, through a pin-hole opened by the screw-valve at *F*, and escapes at *E* after passing up in intimate contact with the coil.

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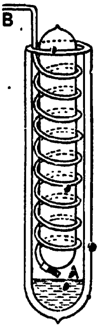
[1] These methods of separation are superseded by an improved method invented later by Linde and described below, pp. 161 *et seq.* (1908.)



SEP. 1922.
BENGAL.

Fig. 57.

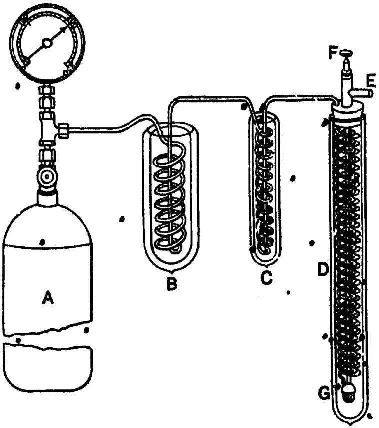


Fig. 58.

Properties of Liquid Hydrogen[1].

Since these lectures were delivered Sir James Dewar has succeeded in obtaining liquid hydrogen in large quantities[2]. He finds it—contrary to the expectation that it would have metallic properties—to be a colourless transparent liquid of extraordinary lightness, with a density about one-fourteenth that of water. Its critical temperature is about − 241° C. By evaporation under reduced pressure it may be frozen into a transparent solid. Its properties are best described in Dewar's own words[3]:

"Liquid hydrogen is a colourless transparent body of extraordinary intrinsic interest. It has a clearly defined surface, is easily seen, drops well, in spite of the fact that its surface tension is only the thirty-fifth part of that of water, or about one-fifth that of liquid air, and can be poured easily from vessel to vessel. The liquid does not conduct electricity, and, if anything, is slightly diamagnetic. Compared with an equal volume of liquid air, it requires only one-fifth the quantity of heat for vaporisation; on the other hand, its specific heat is six times that of liquid air or three times that of water. The coefficient of expansion of the fluid is remarkable, being about ten times that of the gas; it is by far the lightest liquid known to exist, its density being only one-fourteenth that of water; the lightest liquid previously known was liquid marsh gas, which is six times heavier. The only solid which has so small density as to float upon its surface is a piece of pith wood. It is by far the coldest liquid known. At ordinary atmospheric pressure it boils at − 252·5° C. or 20·5 degrees absolute. The critical point of the liquid is from 30 to 32 degrees absolute, and the critical pressure not more but probably less than fifteen atmospheres. The vapour of the hydrogen arising from the liquid has nearly the density of air—that is, it is fourteen times that of the gas at the ordinary temperature. Reduction of the pressure by an air-pump brings down the temperature to − 258°C., when the liquid becomes a solid resembling frozen foam, and this by further exhaustion is cooled to − 259·5°C., or 13½ degrees absolute, which is the lowest steady temperature that has been reached. The solid may also be got in the form of a clear transparent ice, melting at about 15 degrees absolute, under a pressure of 55 mm., possessing the unique density of one-tenth that of water. Such cold involves the solidification of every gaseous substance but one that is at present definitely known to the chemist, and so liquid hydrogen introduces the investigator to a world of solid bodies. The contrast between this refrigerating substance and liquid air is most remarkable. On the removal of the loose plug of cotton-wool used to cover the mouth of the vacuum vessel in which it is stored, the action is followed by a miniature snowstorm of solid air, formed by the freezing of the atmosphere at the point where it comes into contact with the cold vapour rising from the liquid. This solid air falls into the vessel and accumulates as a white snow at the bottom of the liquid hydrogen. When the outside of an ordinary test-tube is cooled by immersion in the liquid, it is soon observed to fill up with solid air, and if the tube be now lifted out a double effect is visible, for liquid air is produced both in the inside and on the outside of the tube—in the one case by the melting of the solid, and in the other by condensation from the atmosphere. A tuft of cotton-wool soaked in the liquid and then held near the pole of a strong magnet is attracted, and it might be inferred therefrom that liquid hydrogen is a magnetic body. This, however, is not the case: the attraction is due neither to the cotton-wool nor to the hydrogen—which indeed evaporates almost as soon as the tuft is taken out of the liquid—but to the oxygen of the air, which is well known to be a magnetic body, frozen in the wool by the extreme cold.

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[1] This and the remaining paragraphs are added in 1908.

[2] *Proceedings of the Royal Institution*, Jan. and June, 1899.

[3] Address as President of the British Association, Belfast, 1902.

"The strong condensing powers of liquid hydrogen afford a simple means of producing vacua of very high tenuity. When one end of a sealed tube containing ordinary air is placed for a short time in the liquid, the contained air accumulates as a solid at the bottom, while the higher part is almost entirely deprived of particles of gas. So perfect is the vacuum thus formed, that the electric discharge can be made to pass only with the greatest difficulty. Another important application of liquid air, liquid hydrogen, &c., is as analytic agents. Thus, if a gaseous mixture be cooled by means of liquid oxygen, only those constituents will be left in the gaseous state which are less condensable than oxygen. Similarly, if this gaseous residue be in its turn cooled in liquid hydrogen a still further separation will be effected, everything that is less volatile than hydrogen being condensed to a liquid or solid. By proceeding in this fashion it has been found possible to isolate helium from a mixture in which it is present to the extent of only one part in one thousand. By the evaporation of solid hydrogen under the air-pump we can reach within 13 or 14 degrees of the zero, but there or thereabouts our progress is barred. This gap of 13 degrees might seem at first sight insignificant in comparison with the hundreds that have already been conquered. But to win one degree low down the scale is quite a different matter from doing so at higher temperatures; in fact, to annihilate these few remaining degrees would be a far greater achievement than any so far accomplished in low temperature research. For the difficulty is twofold, having to do partly with process and partly with material. The application of the methods used in the liquefaction of gases becomes continually harder and more troublesome as the working temperature is reduced; thus, to pass from liquid air to liquid hydrogen—a difference of 60 degrees—is, from a thermodynamic point of view, as difficult as to bridge the gap of 150 degrees that separates liquid chlorine and liquid air."

Liquefaction of Helium.

The liquefaction of helium, the most intractable of gases, is announced by Professor Kamerlingh Onnes of Leyden[1]. He obtained 60 cubic centimetres of the liquid and found that it did not solidify under a pressure reduced to 1 cm. of mercury. Its boiling point is given as 4·5 degrees absolute—a temperature far lower than anything reached before and astonishingly near the absolute zero. Its density is 0·15.

Previous attempts by Olscewski and by Dewar, using sudden expansion after the gas under pressure had been cooled by liquid hydrogen, had been unsuccessful. Dewar had also circulated helium in a counter-current apparatus to obtain cumulative cooling, but he was unable to carry the process far enough through the inadequacy of the supply of the gas.

Occlusion of Gases by Charcoal at Low Temperatures.

Before we leave the subject of low temperature research brief mention may be made of the important property which certain porous bodies and especially charcoal have of absorbing large volumes of gas when the temperature is low. This has been studied by Dewar and applied by him to the production of high vacua[1]. The absorptive power of charcoal at ordinary temperatures has long been known: at extremely low temperatures it is enormously increased. A gramme of charcoal, for instance, which will absorb 18 cubic centimetres of oxygen at 0° C. will absorb 230 cubic centimetres, or nearly 13 times as much, at −185° C. The corresponding number for hydrogen are 4 and 135 at the same two temperatures. This property affords a convenient means of producing the highest degrees of exhaustion and also of separating the less easily absorbed gases, such as helium and neon, from air or other gaseous mixtures.

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[1] *The Times*, July 20 and August 12, 1908.

Further developments of the method of obtaining Oxygen by liquefying air. Rectification.

Thanks to a further invention by Linde the preparation of oxygen by liquefying air has now become a practicable commercial process which is already in use on a large scale and bids fair to make any chemical method obsolete. It enables practically pure oxygen to be obtained at a very moderate cost. By a further extension pure nitrogen may also be obtained, should that product be wanted. The separation of the two constituents of air, which was very imperfect in the earlier process described above, may readily be made as complete as is desired. This highly important practical result has been accomplished by adapting in the treatment of liquid air the process known as *rectification* which has for long been used in distilling, where it is used to extract spirit from the "wash" or fermented wort which is a weak mixture of alcohol and water. In the still patented by Æneas Coffey in 1830, there is a rectifying column consisting of a tall chamber containing many zig-zag shelves or baffle plates. The wash enters at the top of the column and trickles slowly down, meeting a current of steam which is admitted at the bottom and rises up through the shelves. The down-coming wash and the up-going steam are thereby brought into close contact and an exchange takes place. At each stage some of the alcohol is evaporated from the wash and some of the steam is condensed, the heat supplied by the condensation of the steam serving to evaporate the alcohol. The condensed steam becomes part of the down-coming stream of fluid: the evaporated alcohol becomes part of the up-going stream of vapour. Finally at the top a vapour comparatively rich in alcohol passes off: at the bottom a fluid accumulates which is water with little or no alcohol in it. A temperature gradient is established in the column: at the bottom the temperature is that of steam and at the top there is a lower temperature approximating to the boiling point of alcohol. The wash enters at this comparatively low temperature, and takes up heat from the steam as it trickles down.

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[1] *Proceedings of the Royal Institution*, Jan. 1905, and June, 1906.

In Linde's device the same general idea is applied in a most ingenious manner to separate the less volatile oxygen from the more volatile nitrogen, primarily with the object of obtaining oxygen. In the apparatus there is a rectifying column down which liquid air trickles, starting at the top at a temperature a little under -194° C. or 79° absolute, which is the boiling point of liquid air under atmospheric pressure. As this trickles down it meets an up-going stream of gas which consists (at the bottom) of nearly pure oxygen, initially at the temperature of about 91° absolute, that being the boiling point of oxygen under atmospheric pressure. As the gas rises and comes into close contact with the down-coming liquid there is a give and take of substance: at each stage some of the rising oxygen is condensed and some of the nitrogen in the down-coming liquid is evaporated; the liquid also gains in temperature. By the time it reaches the bottom it consists of nearly pure oxygen: the nitrogen has almost completely passed off as gas, and the gas, which passes off at the top, consists very largely of nitrogen. More precisely it consists of nitrogen mixed with about 7 per cent. of oxygen: in other words, out of the whole original oxygen content of the air (say 21 per cent.) two-thirds are brought down as liquid oxygen to the bottom of the column, while one-third passes off unseparated along with all the nitrogen. The oxygen which gathers at the bottom is withdrawn for use and is evaporated in serving to liquefy fresh compressed air, which is pumped into the apparatus to undergo the process of separation. The cold gases which are leaving the apparatus, namely the oxygen which is the useful product, and the nitrogen which passes off as waste gas at the top of the column, are made to traverse counter-current interchangers on their way out, so as to give up their cold very completely to the incoming compressed air which is on its way to be liquefied.

In the diagram, Fig. 59, these counter-current interchangers are omitted for the sake of clearness, but the essential features of the condensing and rectifying apparatus are shown. The figure is based on one given in Linde's patent of June 1902, which

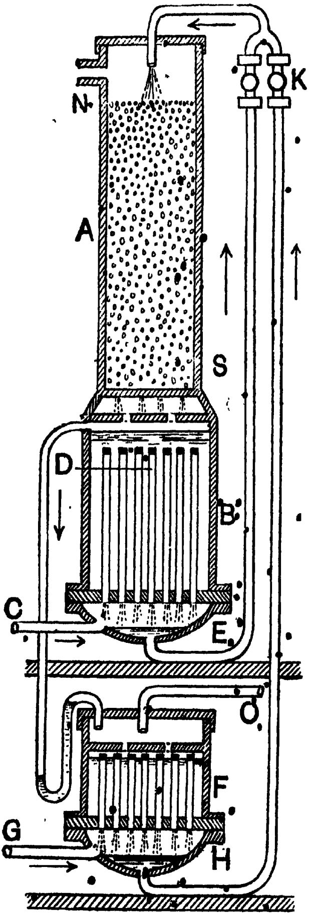

Fig. 59. Linde's apparatus of 1902 for extracting oxygen by rectification.

describes and claims the invention by which the process of rectification has been successfully applied in the extraction of oxygen from air.

There *A* is the rectifying column, consisting in this instance of a vertical chamber stacked with glass balls, through the interstices of which the liquid trickles down. The lower part *B* contains an accumulation of fluid which, when the apparatus has been at work long enough to establish a uniform *régime*, consists of nearly pure liquid oxygen. Compressed air, which has been cooled by passing through a counter-current interchanger, enters at *C*, becomes liquefied in the vertical condenser pipes *D*, which are closed at the top, and drops down into the vessel *E*. It gives up its latent heat to the oxygen in *B*, thereby evaporating a part of that, and so supplying a stream of gaseous oxygen which begins to pass up the rectifying column. On its way up this stream of gas effects an exchange of material with the liquid air which is trickling down: gaseous oxygen is condensed and returns with the stream to the vessel *B*, while nitrogen is evaporated and passes off at the top of the column, at *N*, mixed with some oxygen. The escaping gas goes through the interchanger, giving up its heat to the incoming compressed air.

The accumulation of liquid oxygen in *E* overflows into the lower vessel *F*, where a supplementary supply of compressed air entering at *G* is employed to evaporate it by means of a similar arrangement of condenser tubes open at the bottom and closed at the top, this air becoming itself condensed in the process, and falling as a liquid into the vessel *H*. The condensed air from *F* and from *H* is still under pressure: it passes up through regulating valves *K* to the top of the rectifying column where it is discharged over the glass balls at a pressure not materially above that of the atmosphere. This secures the necessary drop in temperature between the bottom and top of the column, and allows the compressed air to play the *rôle* of heater and evaporator of the liquid oxygen at the bottom at the comparatively high temperature of about 91° absolute before it enters the column. In other words, it not only corresponds to the "wash" of the Coffey still but it also serves as the equivalent of the heater by which the liquid at the bottom of the still gives off an upward current of steam. Gaseous oxygen, the product of the Linde process, passes off at *O*, and the waste gas, consisting mainly of nitrogen, at *N*: they both pass through the counter-current interchanger, giving up their heat to the compressed air which enters partly at *C* and partly at *G*. It is of course the waste gases in this process that form the analogue of the rectified spirit which is the useful product of the Coffey still.

There is no need to let the liquid in *B* overflow into a separate vessel to be evaporated there. The whole of the evaporating process may be carried out in *B* and the vessel *F* may be dispensed with. This is in fact done in the apparatus as it is practically used by the British Oxygen Company. Under these conditions all the compressed air enters at *C* and is condensed in the pipes *D*: part of the oxygen which it evaporates in condensing passes up the column to effect the rectifying action, and the remainder, forming the product of the machine, is allowed to escape through an exit pipe which opens just above the level of the liquid.

In commencing to work the machine the air is highly compressed as in Linde's earlier process, but after the operation has gone on for some time and a steady state is approached a much lower pressure is sufficient. It must of course be high enough to make the air liquefy at the temperature of the liquid oxygen bath, say 91° absolute, and it is in practice kept higher than this to ensure that the drop in passing through the regulating valve may be sufficient to make good thermal losses due to leakage of heat from outside and to imperfect interchange in the counter-current apparatus. The pressure after passing the regulating valve is only some 4 or 5 lbs. per square inch above that of the atmosphere—just enough to cause the gases to escape freely through the counter-current interchanger.

The essential features in this process are (1) that the air to be condensed is first cooled by a counter-current interchanger to a temperature approximating to that of the evaporation products, (2) that it is then caused to give up its latent heat to the evaporating liquid, and (3) that the liquid air is subjected to the rectifying action of vapour from the evaporating liquid.

For some time after the apparatus is first started a high pressure is needed to secure liquefaction of the air, and the rectifying action is imperfect, but as the process goes on the liquid contents of the vessel *B* become richer and richer in oxygen, the rectification becomes more complete, and the pressure may be much reduced. Under practical conditions it is easy to secure that the gaseous product shall be pure to the extent of containing 98 per cent. of oxygen. The working pressure, after a steady condition is reached, is about 50 atmospheres. Initially when the apparatus is started it is about three times this, and the initial stages occupy about three hours, before the steady output begins.

In the process as carried out by the British Oxygen Company the counter-current interchanger takes the form of a compound spiral pipe wrapped round the rectifying column. Fig. 60 is a sectional diagram showing the general arrangement of the pipes. *a, a, a* are three small pipes which convey the compressed air to the apparatus, the whole supply being divided between the three. One of the three is surrounded by a pipe *b* through which the useful product, the oxygen, is led out. The whole set is enclosed in the pipe *c*, through which the waste gases escape. There is a fore-cooler kept cold by means of carbonic acid which cools the compressed air sufficiently to dry it by depositing the moisture before it enters the interchanger, and any carbonic acid in the air is extracted by passing it through slaked lime or a solution of caustic soda before it enters the compressor.

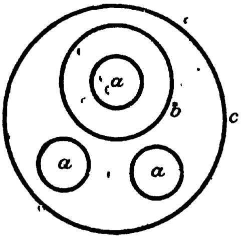

Fig. 60. Arrangement of pipes in counter-current interchanger.

Baly's Curves.

The action of the rectifying column will be made more intelligible if we refer to the results of experiments published in 1900 by Baly*, which deal with the nature of the evaporation in liquid mixtures of oxygen and nitrogen. Given a mixture of these liquids in any assigned proportion, equilibrium between liquid and vapour is possible only when the vapour contains a definite proportion of the two constituents, but this proportion is not the same as that in the liquid mixture. Say for example that the liquid mixture is half oxygen and half nitrogen, then according to Baly's experiments the vapour proceeding from such a mixture will consist of about 22 per cent. of oxygen and 78 per cent. of nitrogen. With these proportions there will be equilibrium. If

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* Baly; *Phil. Mag.*, vol. xlix. p. 517, 1900.

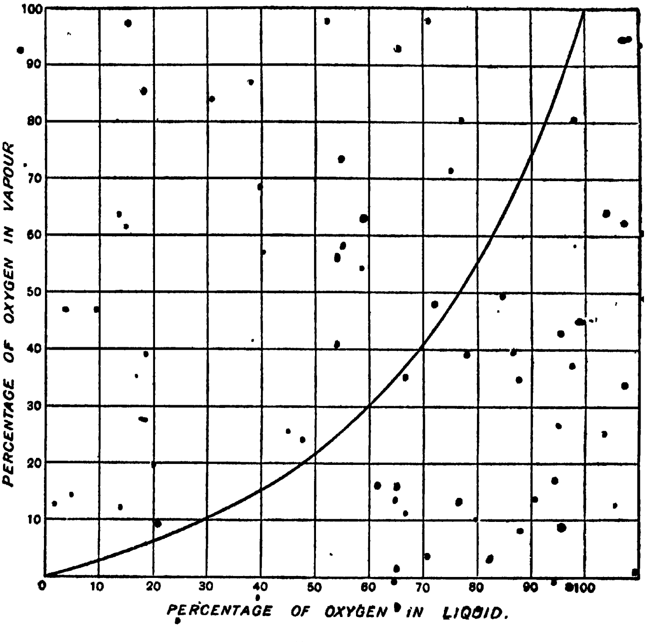

Fig. 61.

however a vapour richer than this in oxygen were brought into contact with the half-and-half liquid, part of the gaseous oxygen would condense and part of the liquid nitrogen would be evaporated until the proportion giving equilibrium were reached. The curve, Fig. 61, shows for each proportion in the mixed liquid what is the corresponding proportion in the vapour necessary for equilibrium: in other words what is the proportion which the constituents have in the vapour when that is being formed by the evaporation of the mixed liquid in the first stages of such an evaporation, before the proportion of the liquid changes. In this curve the base line specifies the proportion of oxygen in the liquid mixture, from 0 to 100 per cent., and the ordinates give the proportion of oxygen in the corresponding vapour when the vapour is formed under a pressure equal to that of the atmosphere. Much the same general relation will hold at other pressures, though the form of the curves may not be quite the same.

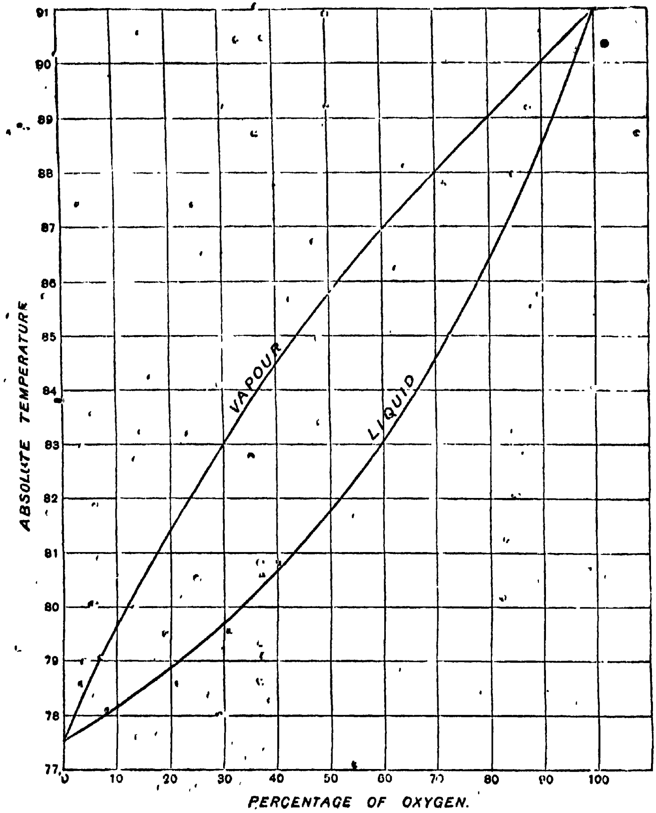

Fig. 62.

It will be seen from this that when the evaporating liquid mixture is liquid air (oxygen 21 per cent., nitrogen 79 per cent.), the proportion of oxygen present in the vapour that is coming off is about 7 per cent. or a little less.

This is what occurs at the top of the rectifying column in Linde's invention, where the liquid that is evaporating is freshly formed liquid air, and hence the waste gases carry off about 7 per cent. of oxygen as has been already stated. Coming down the column the liquid finds itself in contact with gas containing more oxygen than corresponds to equilibrium. Accordingly oxygen is condensed and nitrogen is evaporated at each stage in the descent, in the effort at each level to reach a condition of equilibrium between the liquid and the vapour with which it is there in contact.

Fig. 62 is another form of Baly's curve, the form, namely, in which the results of the experiments were originally shown. There the ordinates represent temperature, namely the absolute temperature (in centigrade degrees) at which, under atmospheric pressure, the mixed liquid boils, and two curves are drawn which show by means of the scale on the base line the percentage constitution of (1) the liquid air, (2) the vapour, when the condition of equilibrium between liquid and vapour is secured[1]. A horizontal line drawn across the curves at any assigned level of temperature shows the composition of vapour and liquid respectively for that temperature, when the two are

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[1] The following figures are given by Baly:

Absolute Temperature	Percentage of Oxygen	
	In Vapour	In Liquid
77·54	0	0
78	2·18	8·10
79	6·80	21·60
80	12·00	33·35
81	17·66	43·38
82	23·60	52·17
83	29·95	59·55
84	36·86	66·20
85	44·25	72·27
86	52·19	77·80
87	60·53	82·95
88	69·58	87·60
89	79·45	91·98
90	89·80	96·15
90·96	100	100

in equilibrium. Taking an intermediate point between the top and bottom of the rectifying column, where the temperature has that value, we should find the respective compositions of liquid and vapour there to approximate to the values found from the two curves, this approximation being closer the more slowly the liquid trickles down and the more intimate the contact between liquid and gas.

If a similar condition of equilibrium holds at each stage in the process of liquefying a mixture of the gases these curves may also be taken as showing what is the proportion of the constituents in the mixed liquid at each stage as condensation of the mixed gas proceeds. Thus when air containing 21 per cent. of oxygen begins to liquefy the liquid initially formed should, under equilibrium conditions, be much richer in oxygen: its proportion according to the curve is 48 per cent.

These conditions are approximately realized when the process known as "scrubbing" is resorted to in the liquefaction of air. By this process, which will be presently described in the form in which it has been practically carried out by Claude, a partial separation between the two constituents is effected during the act of liquefaction.

Complete Rectification.

In Linde's invention of 1902 the rectifying process is incomplete, for although the process yields as pure oxygen as is desired it leaves a part of the oxygen to escape in the waste gas and it does not yield pure nitrogen. In a commercial process for the manufacture of oxygen this is of no consequence: for the raw material costs nothing and the nitrogen is not wanted. But a modification of the process enables separation to be made substantially complete, should it be desired to complete it, and allows approximately pure nitrogen to be obtained, as well as oxygen.

This modification consists in extending the rectifying column upwards and in supplying it at the top with a liquid rich in nitrogen. To do this Linde himself proposed, in 1903[1], to liquefy a portion of the impure nitrogen, which formed the waste gas of the rectifying column, and then to let it trickle down the extended part of the column, to give supplementary rectification. This liquid containing originally say 7 per cent. of oxygen gives off a vapour containing some 2 per cent. only. Hence the process of rectification is at once advanced to a stage which leaves only 2 per cent. of oxygen in the escaping gas; then by condensing some of this gas and using it as the liquid to be supplied at the top of the column a further stage is reached, and so on, until the rectifying process ultimately becomes complete and the escaping product contains practically no oxygen at all.

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[1] British Patent No. 11221, May 1903 (Lightfoot).

In the idea of supplementary rectification by means of a liquid rich in nitrogen Linde was anticipated by a patent of the Société pour l'exploitation des procédés Georges Claude[1]. This patent describes a fractional method of liquefaction which separates the condensed material at once into two liquids, one containing much oxygen and the other little except nitrogen. The latter is sent to the top of the rectifying column, while the former enters the column at a lower point, appropriate to the proportion it contains of the two constituents. Practically pure nitrogen passes off as a gas at the top, and practically pure oxygen from the bottom.

Fig. 63 is a diagram showing this modified process in a form which it took somewhat later[2]. The counter-current interchangers which are of course a part of the actual apparatus are omitted from the diagram.

Compressed air, cooled by the interchanger on its way, enters the condenser at *A*. The condenser consists of two sets of vertical pipes, communicating at the top where they all open into the vessel *B*, but separated at the bottom. The central pipes, which open from the vessel *A*, are one set: the other set form a ring round them and drain into the vessel *C*. Both sets are immersed in a bath, *S*, of liquid which, when the machine is in full operation

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[1] British Patent No. 28682 of 1903, taking date 3 Jan. 1903, that being the date of the first foreign application. The same idea is also found in a patent by R. J. Levy, No. 5649 of 11th March, 1903.

[2] As described by G. Claude in a note communicated to the French Academy of Sciences (*Comptes Rendus*, 20 Nov. 1905). In this note Claude ascribes the earliest suggestion of supplementary rectification by a liquid consisting almost entirely of nitrogen to his colleagues, Messrs Helbronner and Lévy :—

"Je crois intéressant d'ajouter que la première idée de l'épuisement des gaz vaporisés par leur lavage final avec des liquides très pauvres en oxygène, en vue de les ramener à l'état d'azote pur, a été exprimée pour la première fois par mes collaborateurs, MM. A. Helbronner et R. Lévy."

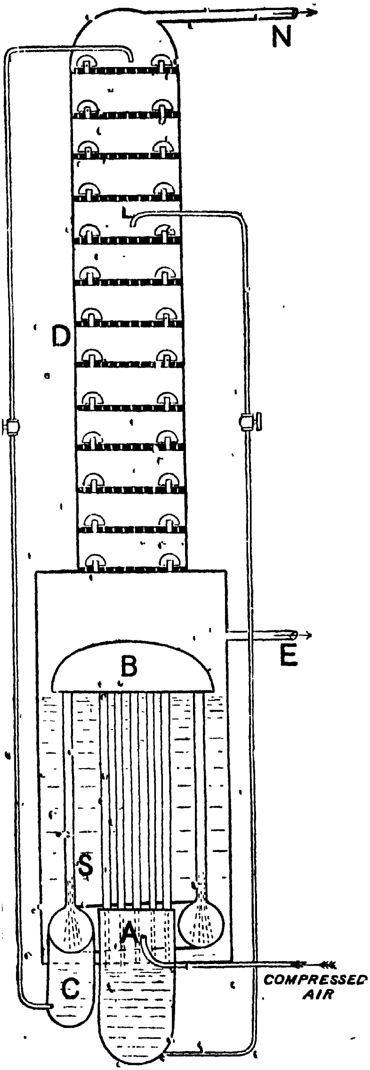

Fig. 63. Claude's apparatus for the complete separation of oxygen and nitrogen.

consists (as in the earlier Linde machine) of nearly pure oxygen. The condensation of the compressed air causes this oxygen to be evaporated. Part of it streams up the rectifying column *D*, to be condensed there in carrying out the work of rectification and consequently to return to the vessel below. The rest of the evaporated oxygen, forming the useful product, goes off by the pipe *E* at the side. In these features the apparatus is substantially the same as Linde's, but there is a difference in the mode of condensation of the compressed air. Entering at *A* it first passes up the central group of condenser pipes and the liquid which is formed in them contains a relatively large proportion of oxygen. This liquid drains back into the vessel *A*, where it collects, and the gas which has survived condensation in these pipes goes on through *B* to the outer set of pipes, is condensed in them, and drains into the other collecting vessel *C*. It consists almost wholly of nitrogen. Then the liquid contents of *C* are taken to the top of the rectifying column, while those of *A* enter the column lower down, at a level *L*, chosen to correspond with the proportion of the constituents. The result is to secure practically complete rectification, and the second product of the machine—commercially pure nitrogen—passes off at the top through the pipe *N* and may be collected for use if desired.

The action in the central pipes of the condenser is to be interpreted in the light of Baly's curves. The first portions of the air to be condensed trickle down the sides of these pipes and are "scrubbed" by the air as it ascends: that is to say they are brought into such intimate contact with the ascending air that a condition of equilibrium between liquid and vapour is at least closely approximated to. The condition of equilibrium when gases of the composition of air are being condensed requires, as we have seen that about 48 per cent. of the liquid should consist of oxygen[1]. Accordingly the liquid which collects in the vessel *A* is of this degree of richness, or near it. And by making the condenser pipes long enough it is clear that little or no oxygen will be left to pass over through *B* into the other pipes. It is true of course that in the upper parts of the central pipes the liquid that is formed consists largely of nitrogen, but as this trickles down the pipe in which it has been condensed there is a give and take between it and the ascending gas, precisely analogous to that which occurs in a rectifying column, and when the liquid reaches the bottom it has been so much enriched in oxygen as to be nearly or completely in equilibrium with the gaseous air, and therefore contains about 48 per cent.

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[1] That proportion, as has been pointed out in speaking of Baly's curves, relates to experiments made at atmospheric pressure. At the higher pressure under which condensation takes place in Claude's apparatus it may not be exactly the same.

When the 48 per cent. liquid from *A* is discharged into the rectifying column at *L* and begins to evaporate it produces an atmosphere which has the composition of air (21 per cent. of oxygen). Hence the part of the column which extends above this point has for its function to reduce the percentage of oxygen in the ascending gas from 21 per cent. to nil, and this is done in the second stage of rectification, by means of the liquid from *C* which consists almost wholly of nitrogen.

Review of stages in the Invention.

To review briefly the chief stages in the invention, as a commercial process for liquefying air and thereby separating its constituents, we have first the invention by Siemens of the counter-current interchanger as a means of reaching an extreme degree of cold by accumulating the effects of a step-down in temperature, which in his case was produced by allowing the air, previously compressed, to expand doing external work. But neither he nor Solvay, who took up the same method later, succeeded in reaching a temperature low enough to liquefy air, being prevented by the practical difficulties of lubricating the expansion cylinder and of keeping the working substance from taking up heat either generated by friction or conducted in from outside the system.

Next came Linde's fundamental invention of 1895, in which the step-down in temperature was achieved without external work, by taking advantage of the Joule-Thomson effect of expansion through a throttle-valve. Combining this step-down with the counter-current interchanger, Linde was successful in liquefying air on a commercial scale and then obtaining, by partial evaporation, a mixture rich in oxygen (in either a liquid or gaseous state) which was put to various practical uses. The result, however, still fell a long way short of yielding commercially pure oxygen, and for that reason had a very limited application.

Seven years later, in 1902, came Linde's brilliant further invention of the rectifying process. By this, for the first time, oxygen in a state of practical purity was obtained commercially from air by a mechanical process at a cost which compared favourably with that of the chemical process formerly in use. The separation of the constituents of air was not, however, complete, the other product being nitrogen with which about 7 per cent. of oxygen was still mixed.

Early in the following year this was followed by the invention of supplementary rectification by means of a liquid rich in nitrogen—an idea which seems to have occurred independently to several inventors (Lévy and Helbronner, Claude, Linde). It enabled complete separation of the constituents to be achieved, yielding as a commercial product practically pure nitrogen as well as practically pure oxygen.

Finally, an apparatus which allowed this supplementary rectification and complete separation to be carried out with great simplicity and effectiveness was devised by Claude, the distinctive feature in it being the fractional condensation of the compressed air. Using a condenser divided into two parts with condenser tubes so arranged as to "scrub" the liquid that is first formed, by making it drain back in contact with the gas which is proceeding to be condensed, Claude collects the liquid in two portions, one of which contains some 48 per cent. of oxygen and the other is almost wholly free from oxygen. By using the two liquids in succession he makes the process of rectification complete.

Commercial Uses of the Products.

It is unnecessary to refer in detail to the numerous commercial uses of oxygen for medical purposes, for the "lime" light and generally for stimulating combustion in metallurgical and other processes. With hydrogen, with coal gas, and more recently with acetylene, it is employed to furnish a blow-pipe flame of very high temperature which finds many engineering applications in welding, patching and so forth. The maximum temperature in the oxy-acetylene flame is estimated to be about 3500° C. A fine jet of oxygen serves as a means of cutting iron by extremely localised fusion when a temperature sufficiently high to start the action has been reached at the place where cutting is begun. A blow-pipe flame, employing any combustible gas such as acetylene or coal-gas, is used in the first instance to heat the metal to redness at the place where it is to be cut, and then the cutting process is carried out by means of a jet of oxygen alone, the metal itself forming the combustible.

An interesting application of the liquid rich in oxygen which Linde obtained in 1895 by the partial evaporation of liquefied air was made by that inventor, in using it mixed with carbon or other combustible matter to furnish an explosive. To make the explosive Linde poured the liquid containing say 50 per cent. of oxygen on fragments of wood charcoal two to four cubic millimetres in size. These were kept from scattering under the ebullition of the liquid by mixing them into a sort of sponge with one-third of their weight of cotton wool. The mixture had to be exploded in a few minutes at most, otherwise its power disappeared through evaporation of the liquid. In more recent experiments conducted in the cutting of the Simplon tunnel this explosive was made up into 3 cm. cartridges: it consisted of one part carbon and one part petroleum and took up about eight parts of liquid oxygen. Such an explosive has the merit of cheapness when it can be made in large quantities and used close to the place of manufacture, but the drawback that it must be used so soon after mixing is probably the chief reason why it has not found any extended employment.

A use which promises to be important has been found for the nitrogen obtained by rectification from liquefied air—namely in the manufacture of calcium cyanamide to serve as an artificial nitrogenous manure, by the process of Messrs Frank and Caro. In that process the cyanamide is formed by passing gaseous nitrogen through retorts containing calcium carbide heated to about 800° C., when the nitrogen is absorbed.

In places where abundance of water power enables the carbide to be cheaply obtained it appears that this nitrogenous manure can be manufactured at a profitable rate, and during the past three years plants for carrying out the process on a fairly large scale have been erected at Piano d' Orta in Central Italy, at Odde in Norway, at Martigny in Switzerland, at Briancon in Savov, and in several other places.

Liquefaction of Air by means of expansion doing work.

It remains only to notice a further invention by Claude which accomplishes the result aimed at unsuccessfully by Siemens and by Solvay. Claude found that the difficulties attendant on expansion in a working cylinder down to a temperature below the critical point of air could be overcome by using certain hydrocarbons as lubricants. A hydrocarbon such as petroleum ether does not solidify but remains viscous at temperatures of −140° or even −160° C. Accordingly it serves as an effective lubricant when its temperature has become reduced to these low levels, and it can also be made to serve in the earlier stages of the operation, when the cylinder is less cold, by mixing it with a greater or less quantity of some more congealable substance such as vaseline.

Using a lubricant of this kind Claude has succeeded, as a *tour de force* of experiment, in liquefying air by direct expansion in a working cylinder. When the liquid begins to form it serves itself as a lubricant and the process may then be continued without introducing any special lubricating material. The efficiency, however, is too low to make this direct liquefaction by expansion commercially useful: the proportion of the quantity of air liquefied to the power expended compares unfavourably with the proportion in Linde's process, where the air does no external work in its expansion. There is in fact very little to be gained by making the gas do work when its condition approximates closely to that of a liquid.

But a much more economical result has been achieved by Claude in another way. He makes part of the compressed air expand in a working cylinder to a temperature which may be just below the critical temperature of air, and he employs the air cooled (but not liquefied) in this way to act as a cooling agent on the remainder of the air, with the result that it is liquefied under the pressure at which it is supplied to the apparatus.

The arrangement in its simplest form is shown diagrammatically in Fig. 64. Air is supplied at a pressure of 40 atmospheres or so through the central pipe of the counter-current interchanger *M*. Part of it passes into the expansion cylinder *D*, where it expands doing work and is then discharged through the condensing vessel *L* where it serves as the cooling agent to maintain a temperature somewhat lower than – 140° C., the critical temperature of air. The remainder of the compressed air enters the tubes of *L* and is condensed there, under pressure, dropping as a liquid into the chamber below from which it can be withdrawn. The temperature in *D* is not allowed at any time to go below the limit at which lubrication can be carried on effectively by using a suitable hydrocarbon.

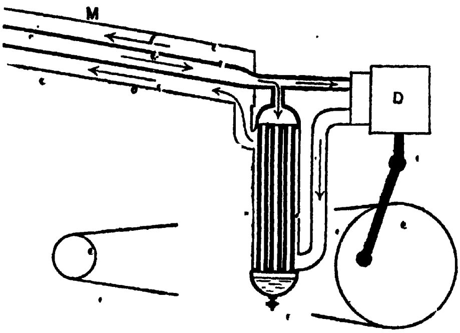

Fig. 64.

In a further development of this invention Claude makes the expansion compound and allows the expanded gas to serve as a cooling agent after each stage, becoming itself warmed up in the process and thereby prepared to suffer further expansion without such an excessive fall of temperature as will endanger lubrication, or bring the gas in the cylinder so near to the liquid state as to make expansion of little use.

The arrangement with compound expansion is illustrated in the diagram (Fig. 65). Air under pressure enters as before, through the central pipe of *M*. Part of it goes to the first expansion cylinder *A*, does work there and passes at reduced pressure and at a temperature below the critical point through the outer vessel of the condenser L_1, in the inner tube of which some of the compressed air is being condensed. This warms up the expanded air to some extent, and it then passes on to complete its expansion in *B*, which again brings its temperature down sufficiently to allow it to act as condensing agent for the remaining portion of the air under pressure, in the second condenser L_2. This division of the expansion into two (or it may be more than two) stages is equivalent to making the process as a whole more nearly isothermal, so that it need not at any stage deviate very widely from a temperature just sufficiently below the critical point to allow liquefaction to go on under the pressure at which the air is supplied.

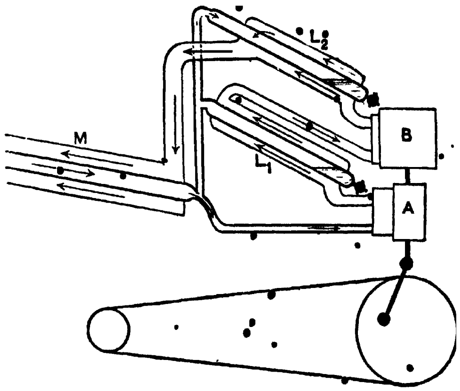

Fig. 65.

In Linde's method of liquefying air without causing it to do any external work the output of liquid air generally ranges from 0·3 to 0·5 litre per horse-power hour. With Claude's device, using a single expansion cylinder, it may be as high as 0·66 and with compound expansion this figure may be raised to 0·85[1]. Treating oxygen as the working substance the output is somewhat greater, and the higher critical point of oxygen (–118° C.) allows expansion to be carried out under somewhat more favourable conditions, by making it unnecessary to continue expansion to so low a temperature as is required in the case of air[2].

So far as concerns the commercial efficiency of processes for the separation of oxygen from nitrogen in air it may be questioned whether there is any very material gain in substituting expansion in a working cylinder for expansion through a throttle-valve. In the initial stages of the operation, while the plant is being cooled down, there may be an economy in its use, but under the conditions of steady output in apparatus of the type represented in Fig. 59 or Fig. 63 it does not appear likely that the advantage to be looked for in the use of expansion with external work can be sufficient to compensate for the added complication in the process.

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[1] Claude, *Comptes Rendus*, 11 June 1906.

[2] Claude, *Comptes Rendus*, 22 Oct. 1906. See also an article by Professor E. Mathias in *Revue générale des Sciences*, 15 Sept. 1907, which contains an interesting account of the whole subject of the industrial liquefaction of air.

APPENDIX A.

Entropy and the Entropy-temperature Diagram.

Let $\delta\phi$ represent the small change in entropy which a substance undergoes in taking in a small quantity of heat δQ at the absolute temperature T. Then by the definition of entropy given in the text, for any reversible change of state,

$$\delta\phi = \frac{\delta Q}{T}.$$

Hence $$T\delta\phi = \delta Q,$$

and $$\int T d\phi = \int dQ,$$

the integration being performed between any assigned limits.

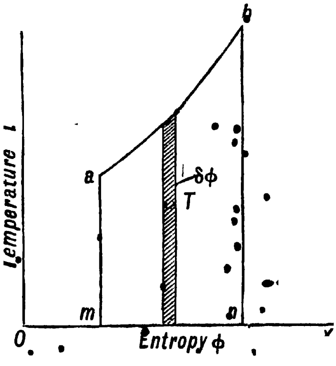

Fig. 66.

Let ab be any portion of a curve drawn with entropy and temperature as coordinates. The narrow cross-hatched strip represents a change $\delta\phi$ occurring at temperature T. Its area is $T\delta\phi$ and is accordingly equal to δQ, the heat taken in while the substance undergoes this change. Summing up the areas of all such successive strips we see that the whole area under the curve or *mabn* represents the whole heat taken in while the substance changes from *a* to *b* through the states which the curve *ab* represents. Similarly, if the substance passes from state *b* to state *a* by a process represented by the line *ba*, it rejects heat equal to the area *nbam*. The base line in the diagram, *OmnX*, corresponds to the absolute zero of temperature.

When an entropy-temperature diagram is drawn for a complete cycle of changes it forms a closed figure, since the substance returns to its original state. To find the area of the figure we have to integrate throughout the complete cycle, obtaining, in any reversible cycle,

$$\int T d\phi = Q_1 - Q_2,$$

where Q_1 is the heat taken in and Q_2 the heat rejected. The difference between these is the heat equivalent to the work spent on the substance, if Q_2 is greater than Q_1, or converted into work if Q_1 is greater than Q_2, since in a complete cycle the equation applies

Heat taken in = heat given out + work done by the substance.

Thus the entropy-temperature diagram has the important property in common with the pressure-volume diagram, that the area of the completely enclosed figure is a measure of work. But this is true only when there is no irreversible step such as expansion through a throttle-valve. In the entropy diagram the work so measured is, of course, expressed in thermal units.

When the substance expands in an *irreversible* manner, as by passing through a throttle-valve from a region of high pressure to a region of lower pressure, it gains entropy. Work is then done by the substance on itself, namely in giving energy of motion to each particle as it passes through the valve, and this energy of motion is frittered down into heat as the motion subsides. We may regard expansion through a throttle-valve as equivalent to two stages, namely (1) expansion doing work, and (2) the communication to the substance of an amount of heat equal to the work done in stage (1) which is to be taken as converted into heat for the purpose. There is accordingly a gain of entropy, though in the result no work is done outside the substance and no heat is rejected or taken in from outside.

APPENDIX B.

Theoretical Performance in the Bell-Coleman Cycle.

The substance takes in heat in becoming warmed from the temperature T_4 (at which it is discharged into the cold chamber after expansion) to the temperature T_1 at which the chamber is maintained. It rejects heat, to the circulating water of the cooler, in passing from the temperature T_2, which it reaches at the end of compression, to T_3. Treating these transfers of heat as, approximately, occurring at constant pressure, and using K_p to denote the specific heat of air at constant pressure, we have

$$\text{Heat taken in, } Q_2 = K_p(T_1 - T_4),$$
$$\text{Heat rejected, } Q_1 = K_p(T_2 - T_3).$$

Further, since the range of adiabatic expansion is the same as that of adiabatic compression,

$$\frac{T_3}{T_4} = \frac{T_2}{T_1}.$$

Hence $\dfrac{T_2}{T_3} = \dfrac{T_1}{T_4}$ and $\dfrac{T_2 - T_3}{T_3} = \dfrac{T_1 - T_4}{T_4}$.

From which $\dfrac{Q_2}{Q_1} = \dfrac{T_4}{T_3} = \dfrac{T_1}{T_2}$.

The theoretical co-efficient of performance in this cycle, which is

$$\frac{Q_2}{W} \text{ or } \frac{Q_2}{Q_1 - Q_2},$$

may accordingly be written

$$\frac{T_4}{T_3 - T_4} \text{ or } \frac{T_1}{T_2 - T_1}.$$

A "perfect" machine, working to transfer heat from the chamber at T_1 to the cooling water at T_3, would have for its coefficient of performance the value

$$\frac{T_1}{T_3 - T_1},$$

which is higher than the theoretical performance in the foregoing cycle, since $T_3 - T_1$ is greater than $T_2 - T_1$. The difference in efficiency arises from the fact that in the Bell-Coleman cycle the air is chilled to a limit considerably lower than that of the cold chamber, and further there is an irreversible flow of heat when the air, after being heated by compression, is brought into contact with the circulating water in the cooler, the effect being to reduce its temperature from T_2 to T_3. This last source of loss may be to some extent removed by cooling the air during compression.

The theoretical ratio of volumes between the compression and expansion cylinders in the Bell-Coleman cycle (assuming the compression and expansion to be adiabatic) is $\frac{V_1}{V_4}$, which is equal to $\frac{T_1}{T_4}$ or $\frac{T_2}{T_3}$. In practice the ratio of volumes is generally about 1·8 to 1, but may be as low as 1·5 to 1.

APPENDIX C.

Actual Performance in Air Machines.

In an early example described by Lightfoot (*Min. Proc. Inst. C. E.* 1881) the following data are stated. The cylinders were 27 and 24 inches in diameter, with a stroke of 18 inches, working at 62 revolutions per minute. The ratio of volumes was accordingly 1·5 to 1. The air was compressed to 65 lbs. absolute. The temperatures were:

On entering compression cylinder	52° Fahr.
On leaving compression cylinder	267° Fahr.
On entering expansion cylinder	70° Fahr.
On leaving expansion cylinder	−82° Fahr.

The indicated H.P. in the compression cylinder was 43·1, in the expansion cylinder 28·0. The difference or net I.H.P. expended was accordingly 15·1, and to provide this (as well as the work spent on friction) the steam cylinder did work at the rate of 24·6 I.H.P. The volume of cold air passed through the machine was 15,000 cubic feet per hour, and its weight was 1620 lbs. It was lowered in temperature from 52° to −82°, or 134° Fahr. Taking the specific heat K_p as 0·2375 this represents a refrigerating effect of 31·85 × 1620 or 50,800 thermal units per hour, which is the heat equivalent of 20 horse-power. If these data are correct it appears that the practical co-efficient of performance was $\frac{20}{24{\cdot}6}$, or nearly 0·8. In a later paper Mr Lightfoot[1] gives data which bring out a co-efficient of 0·7 in the best instances.

In Professor Schröter's trials[2] of a Bell-Coleman machine the results were less favourable. The refrigerating effect in these trials was 0·58, 0·57 and 0·56. The figures in trials by various observers are not very accordant, but it appears that under usual conditions the co-efficient of performance in machines of this class ranges from 0·5 to 0·7, a number which falls very much short of the theoretical figure calculated in the manner described in Appendix B.

APPENDIX D.

Tables of Properties of Ammonia, Sulphurous Acid, Carbonic Acid, and Water Vapour.

In the following tables the figures given by Mollier are followed for the most part[3]. Metric units are employed throughout. They are much the most convenient units to use, especially in calculations regarding theoretical performance. It may be useful to give here a number of constants for conversion to British units.

1 degree C. = 1·8 degrees Fahr.
1 kilogramme = 2·2047 lbs.
1 kg. per sq. cm. = 14·22 lbs. per sq. inc
1 cubic metre = 61,022 cubic inches = 35·316 cubic feet.
1 cubic metre per kilogramme = 27,678 cubic inches per lb.
1 calorie = 3·9685 British thermal units.
1 calorie per kilogramme = 1·8 British thermal units per lb
1 kilogrammetre = 7·2331 foot-pounds.
1 metric horse-power = 4500 kilogrammetres per minute
= 32,549 foot-pounds per minute
= 0·9863 British horse-power.

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[1] *Proc. Inst. Mec. Eng.* 1886.

[2] *Untersuchungen an Kältemaschinen verschiedener Systeme*, i. 1887, p. 165.

[3] "Ueber die kalorischen Eigenschaften der Kohlensaüre und anderer technisch wichtiger Dämpfe." (*Zeitschrift für die gesammte Kälte-Industrie*, 1895.)

Entropy, which has the dimensions of heat per unit mass divided by temperature, is expressed by the same number in both systems of units.

The heat and entropy of the liquid are reckoned as zero at 0° C.; consequently for lower temperatures these quantities are negative in the tables. To find the absolute temperature T add 273 to the temperature on the centigrade scale.

The values of the entropy of vapour (ϕ) and liquid (ϕ') are connected by the equation

$$\phi = \phi' + \frac{r}{T},$$

where r is the latent heat.

Properties of Ammonia (NH_3).

Temp. °C.	Pressure in kg. per sq. cm.	Volume of saturated vapour in cubic metres per kg.	Heat of liquid in calories per kg.	Latent heat of saturated vapour in calories per kg.	Entropy	
					Liquid	Vapour
	p	v	q	r	ϕ'	ϕ
−40	0·72	1·602	−33·36	332·7	−0·132	1·296
−35	0·93	1·257	−29·48	331·8	−0·116	1·278
−30	1·19	0·998	−25·51	330·6	−0·099	1·262
−25	1·51	0·800	−21·47	329·1	−0·083	1·244
−20	1·90	0·646	−17·34	327·2	−0·066	1·227
−15	2·37	0·525	−13·13	324·9	−0·050	1·209
−10	2·92	0·432	−8·13	322·3	−0·033	1·193
−5	3·58	0·358	−4·47	319·4	−0·017	1·175
0	4·35	0·298	0	316·1	0	1·158
5	5·24	0·250	4·54	312·5	0·017	1·141
10	6·27	0·211	9·17	308·6	0·033	1·123
15	7·45	0·180	13·87	304·4	0·050	1·107
20	8·79	0·154	18·66	299·9	0·066	1·089
25	10·31	0·132	23·53	295·0	0·083	1·072
30	12·01	0·114	28·49	289·7	0·099	1·055
35	13·91	0·099	33·52	284·0	0·116	1·038
40	16·01	0·087	38·64	278·0	0·132	1·020

The volume of the liquid (v') may be taken as nearly constant and equal to 0·0016 in cubic metres per kilogramme throughout the range over which the table extends.

In superheating at constant pressure, the specific heat of the gas may be taken as 0·508.

Properties of Sulphurous Acid (SO_2).

Temp. °C.	Pressure in kg. per sq. cm.	Volume of saturated vapour in cubic metres per kg.	Heat of liquid in calories per kg.	Latent heat of saturated vapour in calories per kg.	Entropy	
					Liquid	Vapour
	p	v	q	r	ϕ'	ϕ
−40	0·222	1·305	−11·94	96·10	−0·0472	0·3652
−35	0·297	1·012	−10·55	96·08	−0·0413	0·3624
−30	0·391	0·794	− 9·31	95·89	−0·0354	0·3592
−25	0·508	0·629	− 7·68	95·59	−0·0295	0·3557
−20	0·652	0·503	− 6·20	95·00	−0·0236	0·3519
−15	0·826	0·405	− 4·70	94·30	−0·0177	0·3478
−10	1·037	0·329	− 3·16	93·44	−0·0118	0·3435
− 5	1·287	0·269	− 1·60	92·40	−0·0059	0·3389
0	1·584	0·221	0	91·20	0	0·3341
5	1·932	0·183	1·62	89·83	0·0059	0·3290
10	2·338	0·152	3·28	88·29	0·0118	0·3238
15	2·807	0·127	4·95	86·58	0·0177	0·3183
20	3·347	0·107	6·68	84·70	0·0236	0·3127
25	3·964	0·090	8·42	82·65	0·0295	0·3068
30	4·666	0·076	10·19	80·44	0·0354	0·3009
35	5·458	0·065	11·99	78·05	0·0413	0·2947
40	6·349	0·055	13·82	75·50	0·0472	0·2884

The volume of the liquid (v') may be taken as nearly constant and equal to 0·0007 cubic metres per kilogramme, throughout the range over which the table extends.

Moisture contained in Saturated Air.

Temp. °C.	Moisture in grammes per cubic metre	Temp. °C.	Moisture in grammes per cubic metre
−20	1·10	20	17·18
−15	1·62	25	22·87
−10	2·35	30	30·16
−5	3·41	35	39·46
0	4·88	40	50·96
5	6·81	45	65·19
10	9·37	50	82·68
15	12·78		

Properties of Carbonic Acid (CO_2).

Temp. °C.	Pressure in kg. per sq. cm.	Volume of liquid in cubic metres per kg.	Volume of saturated vapour in cubic metres per kg.	Heat of liquid in calories per kg.	Latent heat of saturated vapour in calories per kg.	Entropy	
						Liquid	Vapour
	p	v'	v	q	r	ϕ'	ϕ
−30	15·0	0·00097	0·0270	−13·78	70·40	−0·053	0·236
−25	17·5	0·00098	0·0229	−11·70	68·47	−0·045	0·231
−20	20·3	0·00100	0·0195	−9·55	66·35	−0·036	0·226
−15	23·6	0·00102	0·0167	−7·32	64·03	−0·028	0·221
−10	27·1	0·00104	0·0143	−5·00	61·47	−0·019	0·215
−5	31·0	0·00107	0·0122	−2·57	58·63	−0·010	0·209
0	35·4	0·00110	0·0104	0	55·45	0	0·203
5	40·3	0·00113	0·0089	2·74	51·86	0·010	0·197
10	45·7	0·00117	0·0075	5·71	47·74	0·021	0·189
15	51·6	0·00123	0·0063	9·01	42·89	0·032	0·181
20	58·1	0·00131	0·0052	12·82	36·93	0·045	0·171
25	65·4	0·00142	0·0042	17·57	28·98	0·061	0·159
30	73·1	0·00167	0·0030	25·25	15·00	0·087	0·136
31	74·7	0·00186	0·0026	28·67	8·40	0·098	0·126
31·35	75·3	0·0022		32·91	0	0·112	

The last line in the table gives the properties of the substance at the critical point.

Properties of Water Vapour.

Temp. °C.	Pressure in kg. per sq. cm.	Volume of saturated vapour in cubic metres per kg.	Heat of liquid in calories per kg.	Latent heat of saturated vapour in calories per kg.
−20	0·00126	994·8	−20·00	620·4
−15	0·00190	666·6	−15·00	616·9
−10	0·00285	451·4	−10·00	613·4
−5	0·00423	307·3	−5·00	610·0
0	0·00625	210·7	0	606·5
5	0·00888	150·2	5·00	603·0
10	0·01245	108·5	10·00	599·5
15	0·01727	79·4	15·00	596·1
20	0·02364	58·7	20·01	592·6
25	0·03202	44·0	25·02	589·1
30	0·04289	33·3	30·03	585·6
35	0·05687	25·4	35·04	582·1
40	0·07470	19·6	40·05	578·6

The volume of the liquid (v') may be taken as nearly constant and equal to 0·001 cubic metres per kilogramme.

APPENDIX E.

Calculation of Theoretical Co-efficient of Performance in Ammonia Cycle, using Adiabatic Compression.

As an example of the calculations, the results of which are stated in the text, take a case where the upper limit is 20° C. and the lower limit −10° C. The corresponding absolute temperatures are 293° and 263°. We shall use metric units (kilogrammes and calories) in the calculation. Neglecting the small term $v'(p_1 - p_2)$, and assuming wet compression, take the net refrigerating effect as the area under *MB*, down to the base line, *minus* the area *ADM*, which may be treated as a triangle.

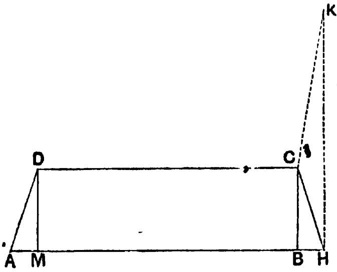

Fig. 67.

In the liquid, the change of entropy per 1° C. is approximately 0·0033. Hence *AM* is 30 × ·0033 = 0·099, and the area

$$ADM = \frac{AM \times MD}{2} = \frac{0{\cdot}099 \times 30}{2} = 1{\cdot}5 \text{ calories.}$$

The change of entropy in passing from liquid to vapour at 20° C., or *DC*, is the latent heat divided by 293 or = 1·023.

Hence $MB = 1{\cdot}023$ and area under $MB = 1{\cdot}023 \times 263 = 269$ calories.

Net refrigerating effect $= 269 - 1{\cdot}5 = 267{\cdot}5$.

Work expended = area $ABCD = AMD + MBCD$

$$= 1{\cdot}5 + 1{\cdot}023 \times 30 = 32{\cdot}2 \text{ calories.}$$

$$\text{Co-efficient of Performance} = \frac{267{\cdot}5}{32{\cdot}2} = 8{\cdot}3.$$

The quantity $v'(p_1 - p_2)$ which is neglected in this calculation of refrigerating effect may be found thus:

Vol. of 1 kilo. of liquid = 0·0016 cubic metres.

$p_1 = 8·8$ kilo. per sq. cm. = 88,000 kilo. per sq. metre.

$p_2 = 2·9$ „ „ = 29,000 „ „

$v'(p_1 - p_2) = 0·0016 \times 59{,}000 = 94$ kilogrammetres = 0·22 calories, a quantity which is practically negligible in comparison with the other quantities involved in the calculation. To take account of it would have the effect of reducing the above co-efficient to about 8·25.

If an expansion cylinder were used, so that the cycle might be completed as in the ideal Carnot process, we should have

Refrigerating effect = area under *MB* = 269·1 calories.

Net work expended = area *MBCD* = 30·7 calories.

$$\text{Co-efficient of performance} = \frac{269}{30·7} = 8·8.$$

Or, more shortly, the co-efficient is in that case

$$\frac{T_2}{T_1 - T_2} = \frac{263}{30} = 8·8.$$

Take next a case where the compression is completely of the "dry" type, the ammonia being allowed to evaporate completely before compression begins. In that case compression starts from *H* (Fig. 67), and the cycle followed is *HKCDA*. The area of that figure is the work expended, and the net refrigerating effect is the area under *AH*, less the area under *AD*, measuring in both cases down to the zero line of temperature.

DC = 1·023, *AH* = 1·226, and *AM* = 0·099. Hence *BH* = 0·104. During a process of superheating at constant pressure, that is between *C* and *K*, the specific heat of the gas is about 0·508 and the change of entropy is approximately ·0017 per degree. Hence in changing its entropy by 0·104 along the line *CK* the gas would be superheated by about $\frac{0·104}{0·0017}$ or 60°. The temperature at *K* is therefore about 80° C. as stated in the text.

To calculate the work expended we have to sum up the areas

$$AMD + BCDM + HKCB,$$

or

$$1·5 + 30·7 + 6·2,$$

the last item being taken as the product of the base 0·104 by the mean height, which is 60°. The total is 38·4. The refrigerating effect is the area under *BF minus AMD*, or

$$(1{\cdot}023 + 0{\cdot}104)\,263 - 1{\cdot}5 = 294{\cdot}9.$$

The co-efficient of performance for completely dry compression is accordingly

$$\frac{294{\cdot}9}{38{\cdot}4} \text{ or } 7{\cdot}7 \text{ nearly},$$

which is not very widely different from the co-efficient 8·3 calculated as above for the "wet" process, notwithstanding the higher temperature reached in compression. The main part of the heat is still rejected at 20°. A similar calculation for a cycle in which the wetness is such that superheating takes place by just half this amount, or by 30° (up to 50° C.) gives a co-efficient of 8·14; and another in which the superheat is only 10° gives a co-efficient of 8·28. These results show how little the co-efficient is affected, in theory at least, by a moderate amount of superheating during compression.

In modern practice the tendency is to use dry compression. As these calculations show, the loss resulting from the substitution of wet for dry compression is small, and there is considerable practical simplification in making the compressor draw in dry vapour instead of a carefully regulated mixture of vapour and liquid.

APPENDIX F.

Mollier's ϕI diagram.

A diagram of great interest which is of special utility in dealing with refrigerating machines employing carbonic acid has been introduced by Dr R. Mollier[1]. The coordinates are the entropy and a quantity to which Willard Gibbs gave the name of "Thermodynamic Potential." We shall represent this quantity by the symbol *I*, and call it the "Total Heat." It may be defined by means of the equation

$$I = E + Apv,$$

[1] "Neue Diagramme zur technischen Wärmelehre," R. Mollier, *Zeitschrift des Vereins deutscher Ingenieure*, 1904.

where E is the internal energy of the substance,
p is the pressure,
v is the volume,
A is the co-efficient required to convert units of work into units of heat, in other words $\frac{1}{J}$. When metric units are used A is $\frac{1}{427}$.

Apply this to the case of a saturated vapour formed under constant pressure p, and take the zero state, for purposes of reckoning, as that of the liquid at 0° C., under the same pressure p[1].

Then E is the total heat taken in, *minus* work done in the expansion of the liquid and the formation of the vapour, or

$$E = q - Ap(v' - v_0') + r - Ap(v - v'),$$

where q = heat taken in during the heating of the liquid,
r = latent heat,
v_0' = volume of liquid at 0° C. and pressure p,
v' = volume of liquid at temperature of vaporization and pressure p,
v = volume of vapour.

Hence $$E = q + Apv_0' + r - Apv,$$
and since $$I = E + Apv,$$
$$I = q + Apv_0' + r.$$

Hence I in a vapour is nearly the same thing as the heat of formation $(q + r)$. It differs from that only by the addition of the small term Apv_0'.

To realise the physical meaning of I, imagine that the conversion of the substance from liquid at 0° to vapour goes on in a cylinder under a piston loaded to produce the constant pressure p. Then to get the liquid into the cylinder in the first place we should have to spend upon it an amount of work equal to this pressure into the original volume v_0'. The thermal equivalent of this work is Apv_0'. Hence I measures the total energy expended in getting the substance into the vessel, and in heating it there until its conversion into vapour is completed.

---

[1] It is assumed here, for the sake of simplification, that any change of I which the liquid at 0° C. undergoes when the pressure is changed from a standard pressure p_0 to the pressure p is so small as to be negligible.

If the conversion into vapour is incomplete, the only difference is that in the process of evaporation the heat taken in is xr instead of r, x being the dryness. Thus for wet vapour

$$I = q + Apv_0' + xr.$$

The value of I for the liquid, at the temperature of vaporization, is $q + Apv_0'$, and during evaporation the value changes in proportion to the amount evaporated.

Using the data for carbonic acid already given in Appendix D, the values of I are as follows, for the two states of liquid and saturated vapour, the difference between the two being equal to r.

Values of I for Carbonic Acid.

Temperature °C.	Liquid	Vapour
−30	−13·39	57·01
−20	−[illegible]·02	57·34
10	− 4·03	57·17
0	0·92	56·37
10	6·90	54·61
20	14·33	51·26
30	27·15	42·15
31·35 (critical temp.)	34·87	

The following are important properties of I, which make it useful in technical thermodynamics;

(1) In any process carried out under constant pressure, the change of I measures the heat taken in or given out. To show this, take the general equation

Heat taken in = increase of internal energy + external work done,

and write δQ to represent a small gain of heat, δE the corresponding gain of internal energy, and δv the change of volume.

Then,

$$\begin{aligned} \delta Q &= \delta E + Ap\delta v \\ &= \delta(E + Apv) - Av\delta p \\ &= \delta I - Av\delta p. \end{aligned}$$

Hence, when p is constant during the change,

$$\delta Q = \delta I$$

and

$$I_2 - I_1 = Q_2 - Q_1,$$

for any two states.

(2) In any adiabatic process the change of I measures the work done. To show this, take the above equation

$$\delta Q = \delta I + Av\delta p.$$

In an adiabatic process $\delta Q = 0$. Hence in such a process

$$\delta I = Av\delta p,$$

$$I_2 - I_1 = A\int_{p_1}^{p_2} vdp.$$

That is to say, the increase in I is equal to the work done upon the substance in taking it in at p_1, compressing it from p_1 to p_2, and discharging it at p_2.

(3) When a substance is throttled by streaming through an orifice such as a regulating valve, there is no change in the value of I.

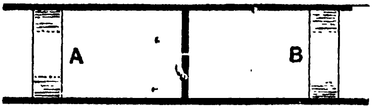

Fig. 68.

Imagine the substance to be transferred from one side to the other of the orifice, by piston A coming up to the orifice while piston B moves away from it. Call the pressure and volume p_1, v_1 before the transfer, and p_2, v_2 after it. Before passing through the orifice the substance has a stock of internal energy which we shall call E_1, and in addition there is work done upon it by piston A equal to p_1v_1.

On the other side it does work against the piston B, equal to p_2v_2. Hence E_2, the stock of internal energy which it has after the passage, is given by the equation

$$E_2 = E_1 + Ap_1v_1 - Ap_2v_2$$

or

$$E_2 + Ap_2v_2 = E_1 + Ap_1v_1,$$

which may be written $I_2 = I_1$.

In other words the quantity I remains unchanged. The imaginary pistons A and B are introduced only to make the argument clear: the result is of general application to all cases of throttling.

Having regard to this result I might be described as that quantity which does not change when a substance expands without doing work and without taking in or giving out heat.

In Dr Mollier's diagram the quantity I is plotted in relation to the entropy ϕ, as the substance changes, under each assigned pressure, from the state of liquid to that of saturated vapour and then through various stages of superheating.

This ϕI diagram is of great service in finding the theoretical performance of a refrigerating machine. In adiabatic processes the entropy is constant: hence such processes are represented by straight lines parallel to one system of ordinates. The work done in the compression cylinder is directly measured by the change of I, that is to say by a length taken along the adiabatic line representing the compression process. The refrigerating effect is directly measured by the change in I which the substance undergoes during evaporation, this being a constant-pressure process in which, as we have seen above, the increase in I is equal to the heat taken in. Similarly, the heat rejected to the cooling water is directly measured by the decrease in I which the substance undergoes after adiabatic compression, up to the regulating valve, this also being a constant-pressure process. In the passage through the regulating valve there is no change in I: this process is accordingly represented in the diagram by a straight line parallel to one axis. The process of evaporation is also represented by a straight line, for it occurs at constant temperature as well as constant pressure, and hence the change of I is not only equal to the heat taken in but is also proportional to the change of entropy, which is the heat taken in divided by the temperature. In symbols, when p is constant,

$$\delta I = \delta Q$$

$$= T\delta\phi,$$

$$\frac{dI}{d\phi} = T.$$

Thus the *slope* of a constant-pressure line on the ϕI diagram is proportional to the absolute temperature and a line representing evaporation is consequently straight, with a slope proportional to the temperature at which the evaporation takes place. Further the segments into which this line is divided at any stage, measured from the ends which mark the beginning and end of evaporation, represent the fraction which exists as vapour and liquid respectively, just as in the entropy-temperature diagram. The whole change in I which the line represents is the latent heat r, and the segment measured from the beginning of the line up to any point represents a proportional change of I, and so measures xr, x being the dryness at that point.

It will be seen that the diagram gives a ready means of determining all the quantities with which we are concerned in a refrigeration cycle. Its special merit lies in the simple manner in which it represents not only the compressing, condensing and evaporating processes, but also the process of streaming through the regulating valve. This last feature gives it an advantage which the entropy-temperature diagram does not possess.

In drawing the ϕI diagram for carbonic acid, Dr Mollier has used the data supplied by Amagat's investigations, and has given not only the boundary curve for the states of liquid and saturated vapour, but also the relation of I to ϕ in various states of superheating, by means of curves of constant pressure and of constant temperature, covering the region beyond the critical point so far as that is required for application to practical problems.

If the diagram were drawn with ordinary rectangular coordinates it would be inconveniently spread out, and to bring it into reasonable compass Dr Mollier adopts the device of shearing it over by using oblique coordinates.

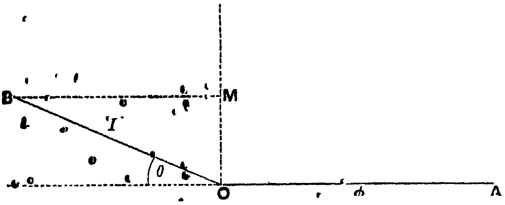

Fig. 69.

Taking the values of entropy along OA (Fig. 69) those of I are taken parallel to an axis OB inclined to AO produced at an angle θ. Values of I may accordingly be measured either along OB, or on another scale along OM (perpendicular to OA). Since $OM = OB \sin \theta$ the scale for measuring I along OM is such that any distance taken along OM represents $\frac{1}{\sin \theta}$ times as many units of I as are represented by the same distance taken along OB.

Dr Mollier's ϕI diagram for carbonic acid, drawn in this manner, is reproduced in Fig. 70, and also on a larger scale in the folding plate at the end of this work. Here $\sin\theta = \frac{1}{5}$ and accordingly the scale for I taken along the isentropic or adiabatic lines (parallel to OB) is five times as coarse as the scale for which figures are given parallel to OM.

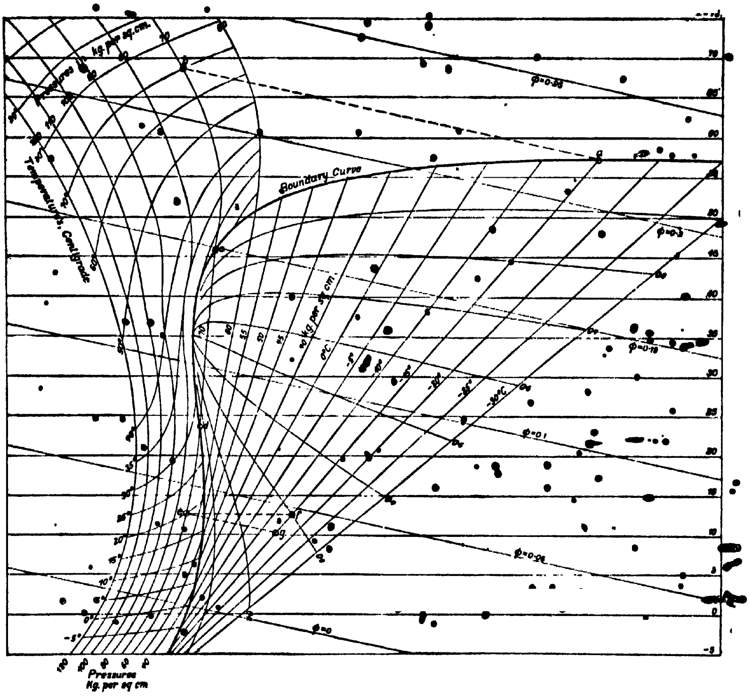

Fig. 70.

The system of parallel lines which run from right to left, sloping upwards, are adiabatics, corresponding to the stated values of the entropy ϕ. A system of horizontal lines is drawn to facilitate measurements of I, using the scale on the right-hand side of the diagram. Any measurements of I taken directly along an adiabatic line are to be interpreted on a scale five times as coarse as this. The straight lines which extend from one side to the other of the boundary curve are lines exhibiting the process of evaporation at the stated temperature (or pressure). As has been shown above the slope of these lines varies from line to line, depending as it does on the temperature.

The curves which lie within the boundary curve are drawn to divide each vaporizing line into ten equal parts, to facilitate reading the proportion of liquid to vapour.

The use of the diagram will be made clear by taking an example (given by Mollier). Suppose evaporation to take place at – 15° C. and to be complete before compression begins. The point (*a*) in Fig. 70 marks the condition of the dry saturated vapour on admission to the compressor. Compression is then carried on till the pressure becomes 70 kg. per sq. cm. This determines the point (*b*) which marks the end of compression and shows that the temperature of the superheated gas is then 70° C. The temperature then falls along a constant pressure line through the point (*b*), and at the point (*c*), when the boundary curve is reached, condensation begins. The temperature at which condensation takes place is the temperature corresponding to a pressure of 70 kg. per sq. cm., namely 28° C. At (*d*) condensation is complete, but in this example it is supposed that the condensed liquid is further cooled to 20° C. before it reaches the regulating valve. This state is marked by (*e*), the line from (*d*) to (*e*) representing the cooling of the liquid still under the constant pressure of 70 kg. per sq. cm. In the passage through the regulating valve i, as we have seen above, is constant: accordingly that process is shown by the horizontal line (*e*) to (*f*). At (*f*) the substance has reached the pressure under which evaporation is to take place, and its wetness, as determined by the segments of the vaporizing line, is 0·3. From (*f*) to (*a*) is the vaporizing process in the evaporator.

The net cooling effect is measured by the change of I during this process, and is therefore given by the vertical distance between (*a*) and (*f*) measured on the scale of I at the right-hand side of the diagram.

The work spent in the compression is measured by the change of I between states (*a*) and (*b*), and is most conveniently found by directly measuring the length (*a*) to (*b*) on the coarser scale for I.

The whole heat given out in the condenser and cooler is measured by the change of I between points (*b*) and (*e*).

Measuring from the diagram, the work done in compression in this example is equivalent to 11·3 heat units; the heat rejected to condenser and cooler is 55·5; the refrigerating effect is 44·2. The co-efficient of performance is accordingly 3·9.

If instead of a regulating valve there were an expansion cylinder, the adiabatic line (*e*) to (*g*) would show the process of adiabatic expansion. Its length would measure (in heat units) the work recovered by the use of the expansion cylinder, and the gain in refrigerating effect would be measured by the difference in *I* between points (*g*) and (*f*). In this example the work saved would be 2·4 heat units, and the refrigerating effect would be increased to 46·6. The theoretical co-efficient of performance would be raised to 5·2. In practice the gain would of course be much less, owing to friction in the expansion cylinder.

The advantage of cooling the liquid as far as possible before it passes the regulating valve is obvious. If this cooling were omitted, and the liquid were to pass through the valve from the state (*d*) the refrigerating effect would be reduced to an extent that is readily found by drawing a horizontal line through the point (*d*) to meet the vaporizing line. The substance after passing the valve would then contain a much smaller proportion of liquid, and the heat to be taken up in completing the evaporation would be correspondingly reduced.

Students of the subject, and especially those who have to do with the design of refrigerating plant using carbonic acid, will do well to master this diagram, which lends itself particularly well to the solution of practical problems. The large scale diagram at the end of the book will be found convenient in such applications[1].

Mollier's *pI* diagram.

Another diagram described by Mollier in the same paper is also interesting and convenient in use. In it the quantities *p* and *I* are taken as rectangular coordinates; horizontal distances represent *I* and vertical distances represent pressure. Lines of constant pressure are therefore horizontal straight lines. The diagram, which is reproduced in Fig. 71, includes a number of isothermals or lines of uniform temperature marked with the temperatures to which they relate, and also a number of adiabatics, toward the right-hand side of the diagram, which are added to facilitate the study of the compression process. The same example as before is represented here, with evaporation occurring at 15° C. Beginning with dry saturated vapour at (*a*), the compression process is *ab*, which goes on till the pressure is 70 kg. per sq. cm. and the temperature is then 70° C. The line *bcde* is the constant pressure process which goes on in the condenser and cooler, namely first cooling to the temperature of the condensation (*bc*), then condensing at that temperature (*cd*), then cooling the condensed liquid to 20° C. (*de*). The line *ef* is the passage through the regulating valve, and *fa* is the evaporation which produces the refrigerating effect. As before, the distance of the point (*f*) from the two limbs of the boundary curve shows the proportion of the substance existing as gas and liquid respectively after passing the regulating valve. A group of curves is drawn, as in the previous figure, within the boundary curve to facilitate the reading of the dryness *x*, by dividing the vaporizing lines into ten equal parts.

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[1] The writer is indebted to Mr Statham of the Linde Company for drawing his attention to the practical advantages of Mollier's diagram, in connection with the design of refrigerating machines, and to Dr Mollier himself for the large diagram reproduced in the folding plate.

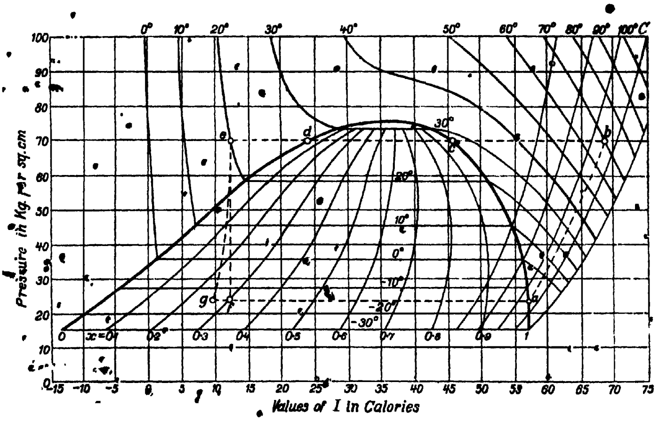

Fig. 71.

The refrigerating effect is directly measured by the length of the line *fa*. The work of compression is the change of *I* between (*a*) and (*b*), which is found by projecting these points on the scale at the foot. The heat rejected to condenser and cooler is then measured by the length *be*. An adiabatic line through (*e*), namely *eg*, is added to show the action that would take place if an expansion cylinder were used instead of a throttle-valve, to let the substance down from the higher to the lower pressure. In that case the refrigerating effect would be increased by the amount *gf*, and this would also measure the work recovered in the expansion cylinder.

The gain in refrigerating effect which results from cooling the condensed liquid as far as the cooling water enables it to be cooled before allowing it to expand is again very apparent.

Compared with the ϕI diagram, the pI diagram affords scarcely so convenient a means of exhibiting and measuring the quantities involved in the refrigerating process, on account of its less simple representation of an adiabatic action, but it has perhaps the advantage of being more easy to understand.

[Note added 1919. For a fuller account of the application of Mollier's ϕI diagram to the action of refrigerating machines of the vapour-compression type, reference should be made to the Report of the Refrigeration Research Committee of the Institution of Mechanical Engineers, published in October 1914.]

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